Decarboxylative Claisen Rearrangement Reactions of Diallyl 2-Sulfonylmalonates: Remarkable Regioselectivity in the Reaction of Bifunctional Substrates

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Keywords

carboxylation, Claisen rearrangement, microwave-assisted synthesis, regioselectivity, substituent effects

Abstract

The decarboxylative Claisen rearrangement of a range of substituted diallyl 2-sulfonylmalonates is described. The reaction displays a very high degree of regioselectivity, with allylic substituents possessing electron-rich substituents at the 3-position rearranging preferentially. The substrates are made by *C*-carboxylation of the corresponding allyl sulfonylacetates with allyl *para*-nitrophenyl carbonates. In one instance, the presence of a highly electron-withdrawing side-chain led to the competing formation of a γ-lactone by-product.

The Claisen rearrangement continues to be the focus of considerable research effort.[1] Since its introduction in 1972,[2] the Ireland silyl ketene acetal variant in particular has been widely used in complex target-oriented synthesis.[3] This modified process benefits from the ease of preparation of the ketene acetal substrates and the relatively mild conditions for the sigmatropic rearrangement. In addition, it enables overall *C*-allylation of carboxylic acids using allylic alcohols as the surrogate electrophiles, with *regiospecific* allylic double-bond transposition. We recently reported[4,5] a novel variant of the Ireland-Claisen rearrangement reaction in which α-tosyl silyl keteneacetals formed in situ from allylic tosylacetates **1** in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and

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potassium acetate undergo thermally-induced [3,3]-sigmatropic rearrangement followed by acetate-induced desilylation-decarboxylation to provide homoallylic sulfones **2** in a single step.[6,7] Furthermore, we have subsequently shown[8] that introduction of an additional electron-withdrawing α-substituent enables malonyl substrates **3** to undergo this decarboxylative Claisen rearrangement (dCr) to provide α-carboxyhomoallyl sulfones **4** at ambient temperature (Scheme 1).

We became interested in the properties of fully bifunctional 2-tolylsulfonylmalonyl dCr substrates such as **5**. These diallyl esters are in principle able to undergo two dCr reaction cycles within the same molecule. We reasoned that dCr substrates such as **5** would be induced to form "monorearrangement" products **6** when subjected to the mild reaction conditions shown to be effective for substrates **3** (Scheme 2). Further reaction of **6** was not expected, since although sulfonylacetates **6** are themselves substrates for a second dCr reaction cycle, they lack the additional electron-withdrawing α-substituent necessary for reaction at ambient temperature. Intramolecular competition experiments have been reported previously[9,10,11,12,13] for the Claisen and related rearrangements. However, the substrates utilised possessed a single ester grouping, which was derived from a doubly-allylic secondary alcohol. Additionally, competition in the decarboxylative variant has not been studied to date.

Previously,[8] 2-tolylsulfonylmalonate dCr substrates **3** were synthesised by sulfonylation of the corresponding malonates with tosyl fluoride under basic conditions at high concentration. In this instance, not all desired dCr substrates **5** were accessible by this route. Therefore we adopted an alternative synthetic approach, employing *para*-nitrophenyl carbonates **7** for the *C*-carboxylation of tosylacetates **1**, to provide diallyl 2-sulfonylmalonates **5** (Scheme 3, Table 3). Both coupling partners **1** and **7** were readily synthesised from the requisite allyl alcohols and commercially-available starting materials (Schemes 4 & 5, Tables 1 & 2). This carboxylation methodology has been shown to be applicable to a variety of R-groups. However, when a highly electron-withdrawing R-group was employed, in addition to the expected product **5g**, the formation of γ-lactone **11** was observed. (Scheme 6). The structure of this by-product has been confirmed by X-ray

crystallography[14] (Figure 1). Lactone **11** is presumed to arise from intramolecular Michael addition of the 2-sulfonylmalonyl enolate to the *para*-nitrostyryl group.

With a variety of dCr substrates **5** in hand, we undertook the study of their rearrangement behaviour. Substrate **5b** underwent smooth dCr reaction at 25 °C in 2 h, furnishing in high yield a diastereomeric mixture (*ca.* 1:1) of rearrangement products **6b** *as a single regioisomer* (Scheme 7). That the products were those of methoxycinnamyl sidechain rearrangement was confirmed by X-ray crystallographic analysis[14,15] of one of the diastereomers (Figure 2). Encouraged by this complete regioselectivity, we explored the rearrangement reactions of substrates **5a** and **5c–h** (Scheme 2). The results are shown in Table 4.

Several features of these results merit comment. Foremost, the remarkable regioselectivity observed for substrate **5b** operates for many of the other substrates also. The only substrates for which total regioselectivity was not observed were **5d** and **5g**. In these instances the phenyl-substituted side chain was the more reactive, as determined from the product ratios (**6d**:**6d'** and **6g**:**6g'** were both 3:1). Overall, a pronounced preference for the reaction of electron-rich side-chains was observed. The most reactive substrate was **5a**, which possesses the most electron-rich allyl groups; this was converted into **6a** in near-quantitative yield at 0 °C. As indicated in Table 4, substrates with less electron-rich side chains required higher reaction temperatures and longer reaction times, and yields of **6** were lower. In the most extreme instance, substrate **5h** was found to be inert to the previous reaction conditions, and use of microwave irradiation was necessary to induce rearrangement, giving **6h** in modest yield.

It seems likely that dCr reaction selectivity is influenced by steric as well as electronic factors. For example, the unexpected skipped diene product **5c**, in which conjugative stabilization has been lost, may arise from the less sterically congested of the two possible regioisomeric transition states. The electronic effect is demonstrated unambiguously by substrates **5b** and **5g**, in which differing aryl *para*- substituents are distant from the reactive array and therefore will not sterically influence the regioselectivity. We are currently engaged in a quantitative kinetic study of these effects. A

comparison of **6e**, **6f** and **6g** suggests the non-reacting side-chain is a determinant of yield (as all three products share the same reacting side-chain). However, variation in yield may simply be due to harsher reaction conditions degrading the substrate/catalyst, or inherent instability of the substrate itself (**6g**, *c.f.* **11**). The results in Table 4 permit the side-chains to be ranked in order of reactivity, as shown in Scheme 8.

The regioselectivity observed for substrates **5f** and **5h** initially seems anomalous. If the diene side-chain in **5c** is more reactive than a phenyl-substituted side-chain, one might expect the enyne side-chain in **5f** and **5h** to react in preference to a phenyl-substituted or unsubstituted side-chain, respectively. However, this was not observed. The alkyne itself is sterically insignificant and we ascribe the lack of reactivity to the trimethylsilyl group instead – the electron-withdrawing nature of silicon biases the electronic distribution so as to disfavour reaction.

A precedent does exist for rate enhancement in the Ireland–Claisen rearrangement with an electron-donating substituent in the C_6 position – Curran has shown[16] that the presence of an oxygen in this position leads to a rate acceleration effect of one or more orders of magnitude. This effect (which has been studied computationally[17]) is rationalized as a "vinylogous anomeric" ($\pi \rightarrow \sigma^*$) stabilization[16d,18] of the transition state, in that weakening of the O_3–C_4 bond facilitates its cleavage upon going to an early transition state[19,20] in which bond-breaking may be[21] significantly more advanced than bond-making (Scheme 9). The observations that an oxygen at the C_4 position leads to a similar rate acceleration[16e] and that solvent effects[16e,20c] and H-bonding additives[16f] are significant further support the idea of a dipolar transition state. Such an argument could equally be applied to our substrates **5a-b**, albeit with the conjugated oxygen further removed from the reactive array. However, our results demonstrate that the effect is by no means limited to oxygen, or indeed any heteroatom; any electron-donating substituent confers enhanced reactivity.

In summary, electronic selectivity of the decarboxylative Claisen rearrangement in bifunctional substrates has been demonstrated. Current studies in our laboratory are directed towards effecting the double rearrangement of diallyl 2-sulfonylmalonates **5** and employing the

resultant dienes in the synthesis of carbocyclic and heterocyclic natural and unnatural products. The results of these investigations will be reported in due course.

Supporting Information

Full experimental details and spectroscopic information are provided for all novel compounds (**1a-g**, **5a-h**, **6a-h**, **7a**,**d**).

Acknowledgements

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[15] The structure was solved for the more crystalline diastereoisomer of **6b**, which was crystallised selectively. In general, mono-dCr reaction of substrates **5** gave products **6** in diastereoisomeric ratios between 1:1 and approximately 2:1.

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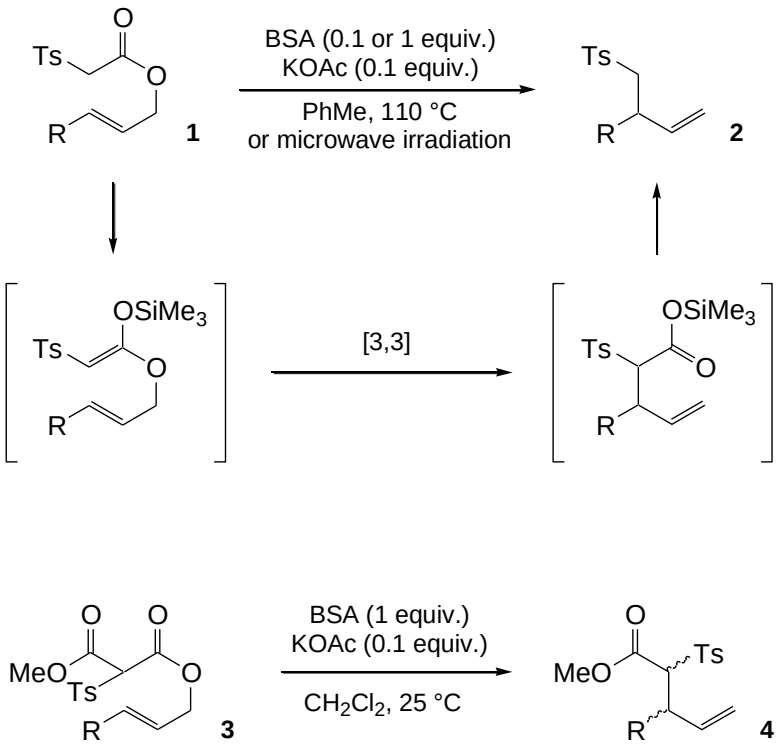
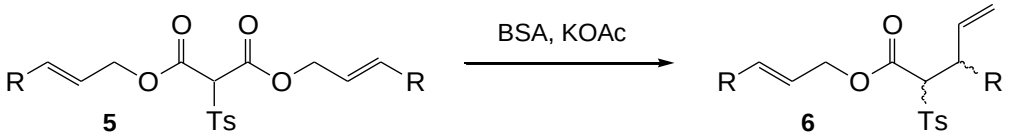
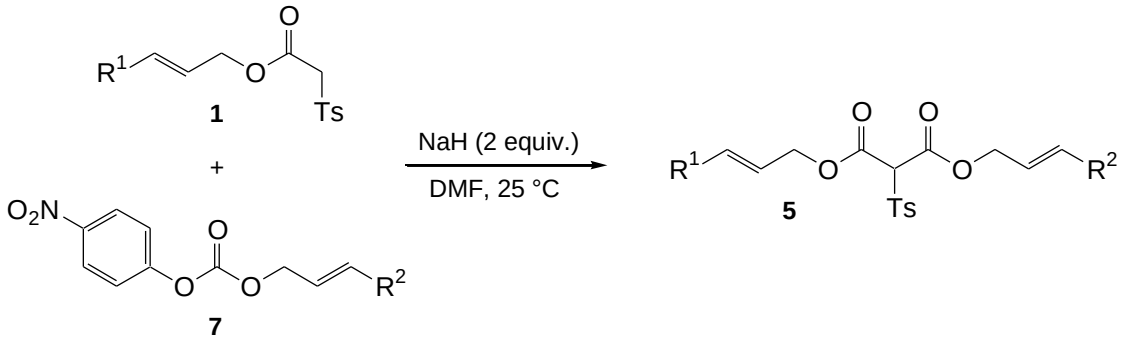


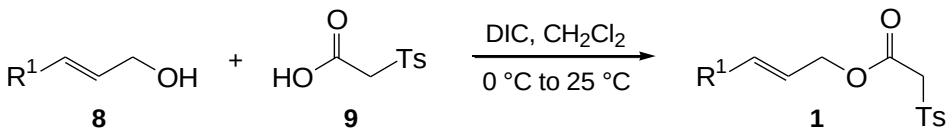
Scheme 1 Synthesis of homoallylic sulfones by the decarboxylative Claisen rearrangement.



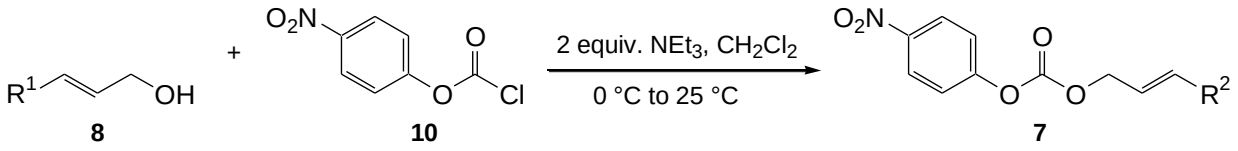
Scheme 2 Reaction of diallyl 2-sulfonylmalonates.



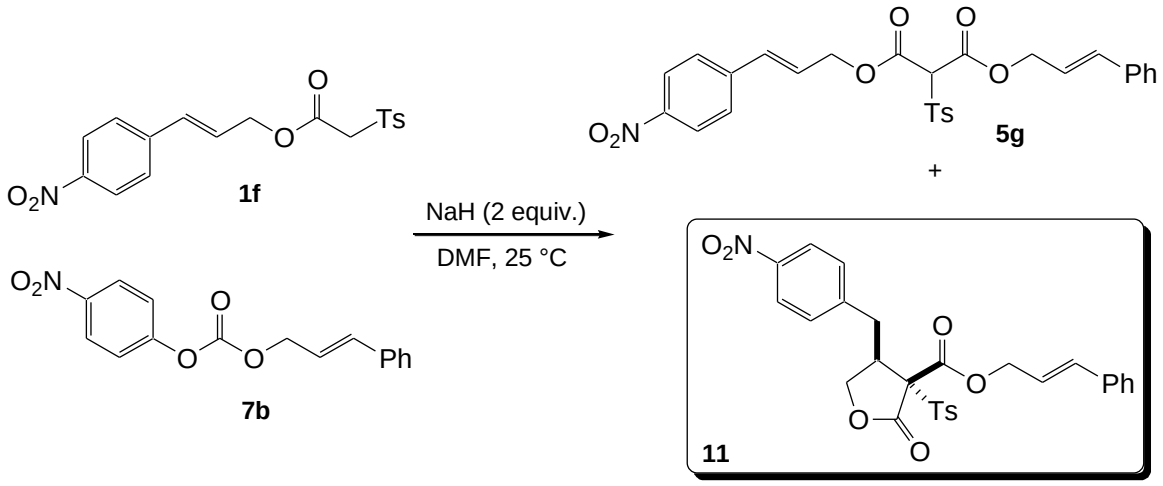
Scheme 3 Synthesis of 2-sulfonylmalonates by *C*-carboxylation.



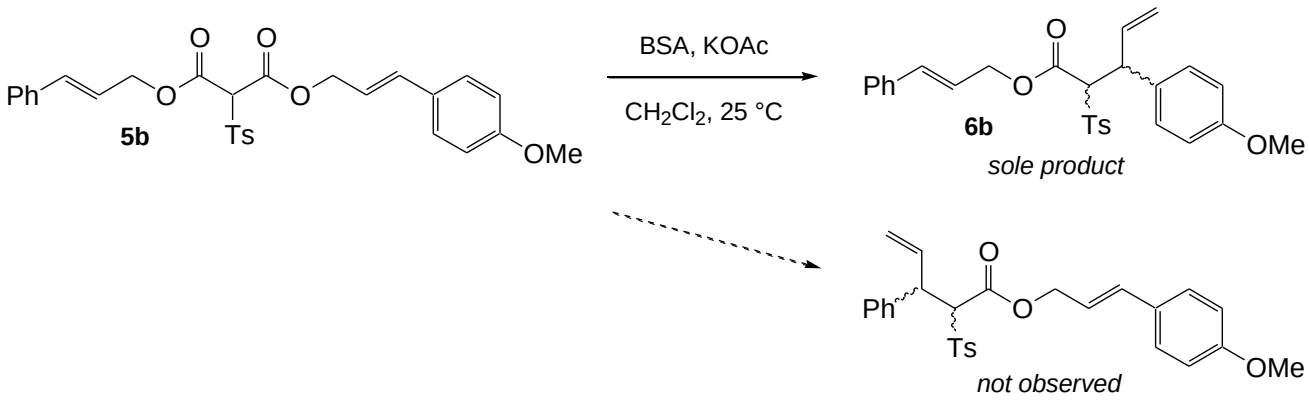
Scheme 4 Synthesis of allyl tosylacetates.



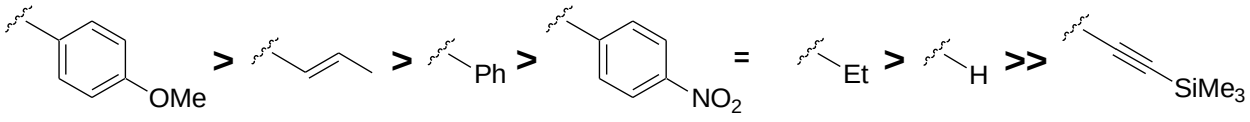
Scheme 5 Synthesis of *p*-nitrophenylcarbonates.



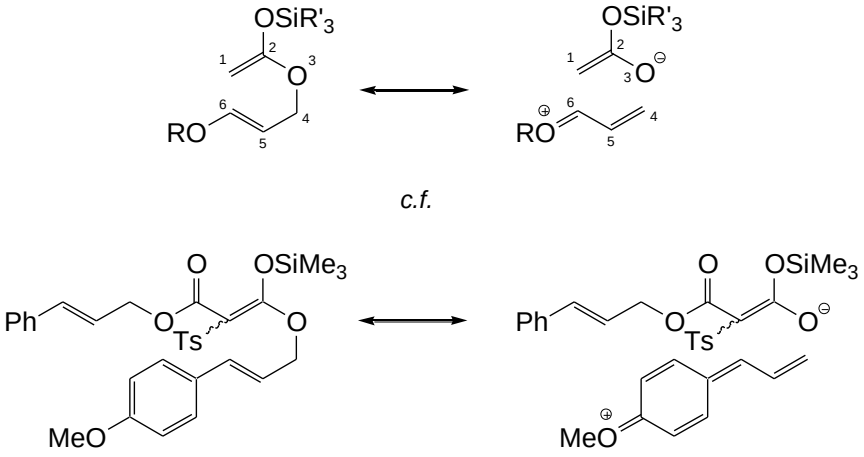
Scheme 6 Unexpected γ-lactone byproduct formation



Scheme 7 Total regioselectivity was observed in the dCr reaction.



Scheme 8 Order of reactivity for side-chains in dCr reaction.



Scheme 9 Proposed vinylogous anomeric effect for 6-oxy substituents.

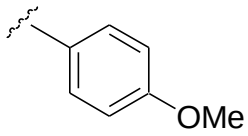
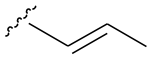
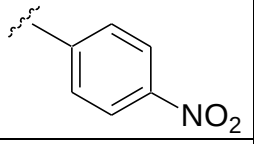
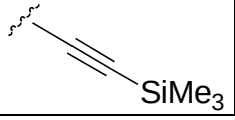
Product	R^1	Yield
1a		76%
1b		87%
1c	Ph	71%
1d	Et	91%
1e	H	92%
1f		94%
1g		65%

Table 1 Yields of allyl tosylacetates

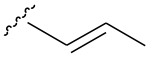
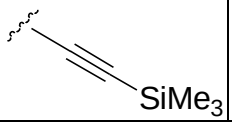
Product	R^1	Yield
7a		76%
7b	Ph	86%
7c	H	91%
7d		75%

Table 2 Yields of *p*-nitrophenylcarbonates

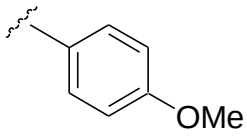
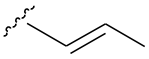
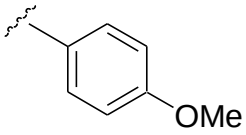
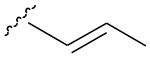
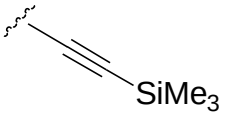
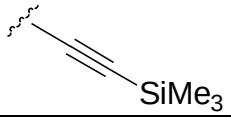
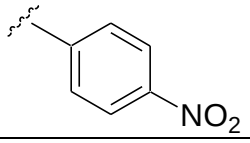
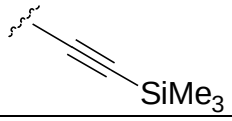
Product	R^1 (Tosylacetate fragment)	R^2 (*p*-nitrophenyl fragment)	Yield
5a			16%
5b		Ph	39%
5c		Ph	30%
5d	Et	Ph	46%
5e	H	Ph	56%
5f	Ph		2%
5f		Ph	28%
5g		Ph	23%, *also 35%* **11**
5h		H	17%

Table 3 Yields of 2-sulfonylmalonates

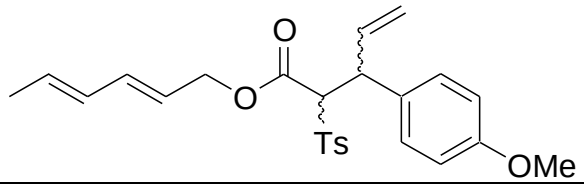
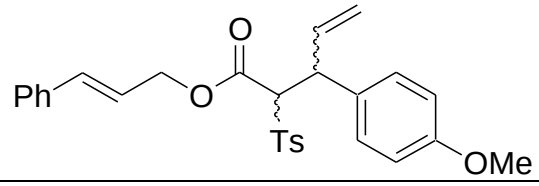
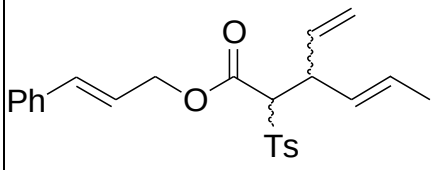
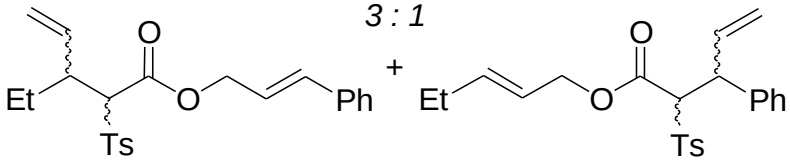
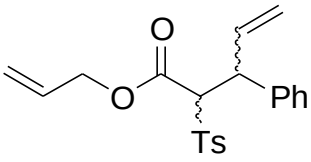
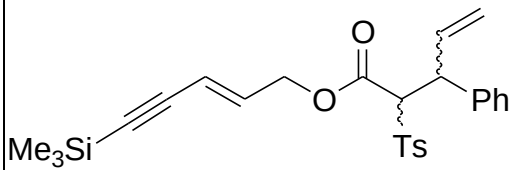
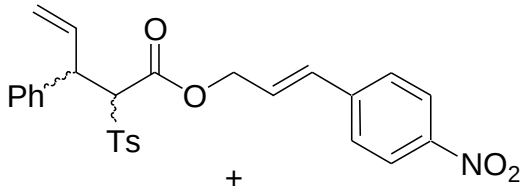
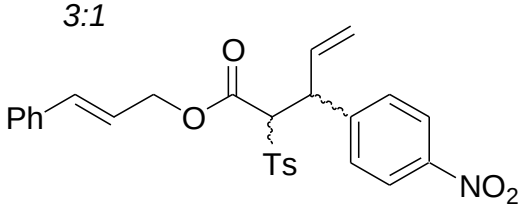
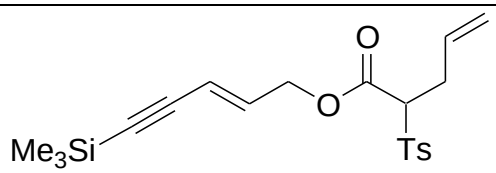
Substrate	Product	Conditions	Yield
5a	**6a** 	CH_2Cl_2, 0 °C, 2 h, 1.0eq. BSA, 0.1eq. KOAc	95%
5b	**6b** 	CH_2Cl_2, 25 °C, 2 h, 1.0eq. BSA, 0.1eq. KOAc	81%
5c	**6c** 	CH_2Cl_2, 25 °C, 16 h, 1.0eq. BSA, 0.1eq. KOAc	79%
5d	*3 : 1*  **6d**	PhMe, 55 °C, 4 h, 2.0eq. BSA, 0.1eq. KOAc	84%
5e	**6e** 	PhMe, reflux, 16 h, 2.0eq. BSA, 0.1eq. KOAc	66%
5f	**6f** 	CH_2Cl_2, 25 °C, 16 h, 1.0eq. BSA, 0.1eq. KOAc	82%
5g	 *3:1*  **6g**	CH_2Cl_2, 25 °C, 16 h, 1.0eq. BSA, 0.1eq. KOAc	29%
5h	**6h** 	CH_2Cl_2, μw, 130 °C, 5 min, 2.0eq. BSA, 0.1eq. KOAc	26%

Table 4 Products formed in dCr reactions

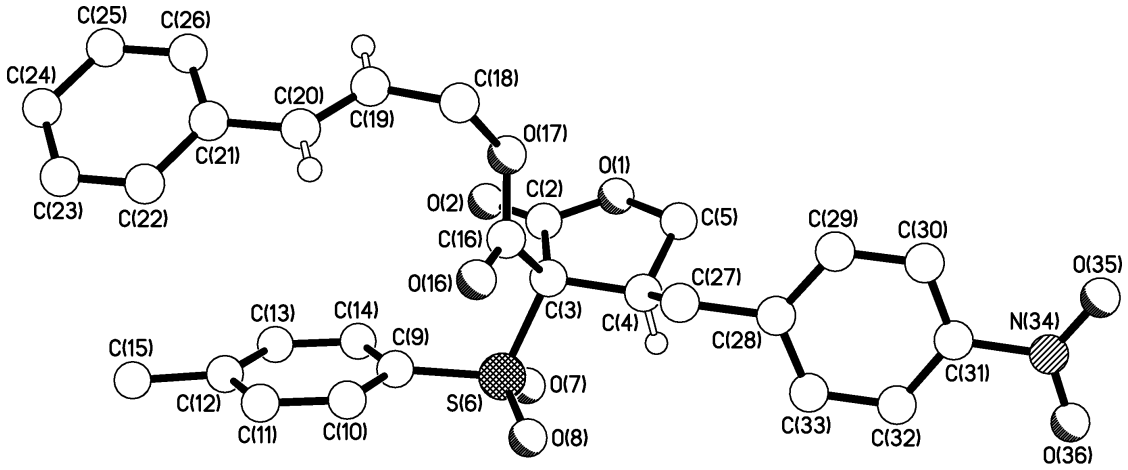


Figure 1 The molecular structure of **11**

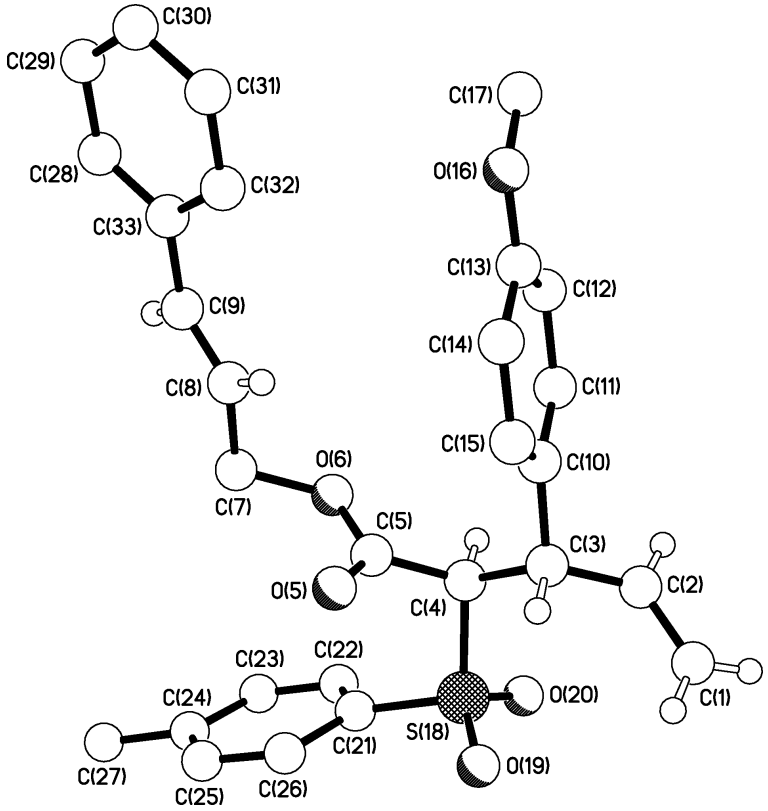
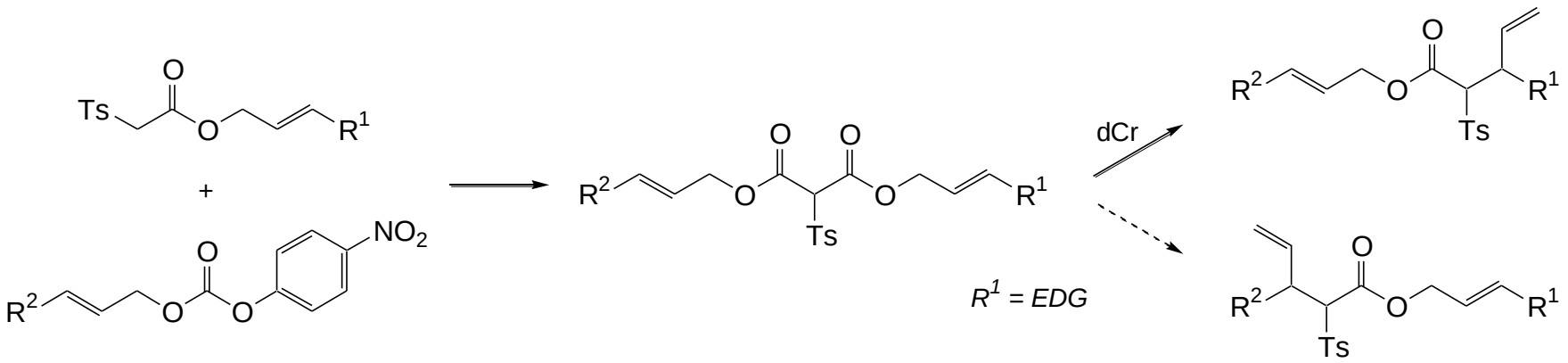


Figure 2 The molecular structure of **6b**

Graphical Abstract

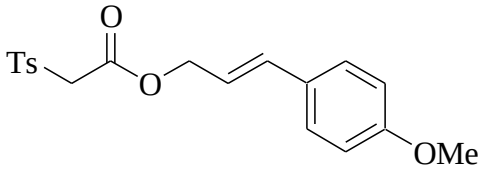
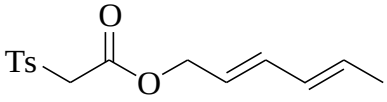
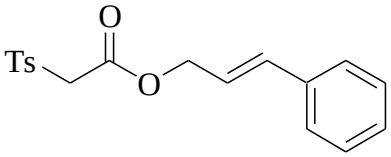
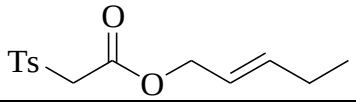
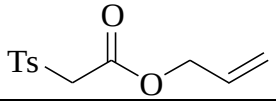
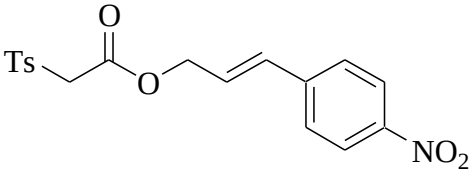
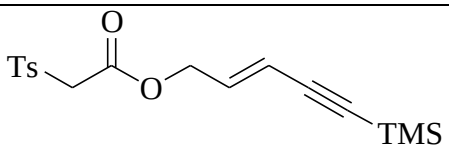


SUPPORTING INFORMATION TO BE PUBLISHED ELECTRONICALLY

General Laboratory Procedures

All reactions were performed under nitrogen unless otherwise stated. Melting points were determined using Stuart Scientific SMP1 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Mattson 5000 FTIR spectrometer. Proton magnetic resonance (^{1}H NMR) spectra and carbon magnetic resonance (^{13}C NMR) spectra were recorded on a Brüker DRX-300, a Brüker DRX-400, a Brüker Avance 400 or a Brüker AM500 spectrometer. Chemical shifts are in parts per million (ppm) and are referenced relative to the residual proton-containing solvent (^{1}H NMR: 7.27 ppm for $CDCl_3$; ^{13}C NMR: 77.0 ppm for $CDCl_3$). Mass spectra (CI, FAB, ESI) were recorded using VG-7070B, VG707E, VG Autospec Q, Brüker Apex II FTICR or Jeol SX-102 instruments. Elemental analyses were performed at the microanalytical laboratory of Dr. Stephen Boyer, London Metropolitan University or by Exeter Analytical Ltd, Brunel Science Park, Uxbridge. Analytical thin layer chromatography (TLC) was performed on precoated aluminium-backed Merck Kieselgel 60 F_{254} plates. Visualisation was effected with ultraviolet light or potassium permanganate. Flash chromatography was performed using BDH (40–63 μm) silica gel. Standard solvents were distilled under nitrogen prior use; Et_2O from sodium-benzophenone ketyl, CH_2Cl_2 from CaH, toluene from sodium. Petrol refers to the fraction bp_{760} 40–60 ^oC. DMF was supplied by Fluka, >99.5% pure, over molecular sieves (<0.005% H_2O). Potassium acetate was oven-dried at 120 °C for several days prior to use. *N*,*O*-bis(trimethylsilyl)acetamide was handled under nitrogen. Sodium hydride was a 60% w/w dispersion in mineral oil. Microwave reactions were performed in a Biotage Initiator.

Monoesters (**1**)

Monoester (*yield)*	Structure
1a (*76%*)	
1b (*87%*)	
1c (*71%*)	
1d (*91%*)	
1e (*92%*)	
1f (*94%*)	
1g (*65%*)	

General procedure (1) for the synthesis of (*p*-Toluenesulfonyl)acetic acid allyl esters (1a-g)

To *desired 3-substituted allyl alcohol* (1.0 equiv) under N_2 was added tosylacetic acid (1.0 equiv) in CH_2Cl_2 (0.2 M). The reaction mixture was cooled to 0 °C and *N,N'*-diisopropylcarbodiimide (1.0 equiv) was added via syringe. The reaction mixture was stirred at 0 °C for 1 h then at rt for 15 h or until TLC indicated reaction completion. The reaction mixture was filtered and concentrated under reduced pressure. Chromatography (EtOAc-petrol) afforded the (*p*-toluenesulfonyl)acetic acid allyl ester in good yield.

(*E*)-4-Methoxycinnamyl (toluene-4-sulfonyl)acetate 1a: *p*-Methoxycinnamyl alcohol (4.59 g, 28.0 mmol), *p*-toluenesulfonylacetic acid (5.99 g, 28.0 mmol) and *N,N'*-diisopropylcarbodiimide (4.38 ml, 28.0 mmol) in CH_2Cl_2 (140 ml) were employed in general procedure **1**. Chromatography (35:65 EtOAc:petrol) gave **1a** (7.66 g, 76%) as a white crystalline solid; m. pt. 81 °C; R_f 0.59 (50:50 EtOAc:petrol); ν_{max} (film) 3033, 2941, 2839, 1739, 1606, 1512, 1456, 1400, 1327, 1275, 1250, 1177, 1149, 1084, 1032, 966, 843, 814, 727, 646 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 2.41 (s, 3H, Ts-CH_3), 3.84 (s, 3H, -O-CH_3), 4.14 (2H, s, -SO_2-CH_2-), 4.73 (d, $^3J_{H,H}$ = 6.5 Hz, 2H, -O-CH_2-), 6.02 (dt, $^3J_{H,H}$ = 16.0, 6.5 Hz, 1H, Ar-CH=C*H*-), 6.57 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, Ar-CH=), 6.89 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *o*-MeO-Ar), 7.28-7.33 (m, 4H, other Ar-H), 7.82 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 21.7 (Ts-CH_3), 55.3 (-O-CH_3), 61.2 (-SO_2-CH_2-), 67.0 (-O-CH_2-), [114.1, 119.3, 128.0, 128.7 and 129.8] (3°), 130.6 (4°), 135.3 (3°), [135.7, 145.4, 159.9 and 162.4] (4°); *m/z* (CI) 378 $[M+NH_4]^+$, 352, 314, 236, 224, 188, 147, 121 (Found: $[M+NH_4]^+$, 378.1379. $C_{19}H_{20}O_5S$ requires $[M+NH_4]^+$, 378.1375) (Found: C, 63.37; H, 5.70. $C_{19}H_{20}O_5S$ requires C, 63.32; H, 5.59%).

(2*E*,4*E*)-Hexa-2,4-dienyl (toluene-4-sulfonyl)acetate (1b): (2*E*,4*E*)-Hexa-2,4-dien-1-ol (1.96 g, 20 mmol), *p*-toluenesulfonylacetic acid (4.29 g, 20 mmol) and *N,N'*-diisopropylcarbodiimide (3.13ml, 20 mmol) were employed in general procedure 1. Chromatography (30:70 EtOAc:petrol) gave **1b** (5.12 g, 87%) as a yellow oil; R_f 0.18 (20:80 EtOAc:petrol); ν_{max} (film) 3005, 2941, 1741, 1703, 1597, 1446, 1440, 1381, 1329, 1304, 1277, 1151, 1086, 991, 814, 727, 646 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 1.73 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, =CH-C*H*$_3$), 2.40 (s, 3H, Ts-CH_3), 4.52 (d, $^3J_{H,H}$ = 6.5 Hz, 2H, -O-CH_2-), [5.38-5.48 and 5.67-5.75] (m, 2H, other olefinic H), 5.97 (dd, $^3J_{H,H}$ = 15.0,

10.5 Hz, 1H, -O-CH_2-CH=CH-C*H*=), 6.15 (dd, $^3J_{H,H}$ = 15.0, 10.5 Hz, 1H, -O-CH_2-CH=C*H*-CH=), 7.31 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-SO_2-Ar), 7.77 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 18.2 (=CH-*C*H_3), 21.7 (Ts-CH_3), 61.0 (-SO_2-*C*H_2-COO-), 66.6 (-O-CH_2-), [122.2, 128.6, 129.8, 130.2 and 131.9] (3°), 135.7 (4°), 135.9 (3 °C), 145.4 (4°), 162.3 (C=O); *m/z* (CI) 606 $[2M+NH_4]^+$, 312 $[M+NH_4]^+$, 188, 115, 98, 81, 64 (Found: $[M+NH_4]^+$, 312.1265. $C_{15}H_{18}O_4S$ requires $[M+NH_4]^+$, 312.1263).

Cinnamyl (toluene-4-sulfonyl)acetate (1c): Cinnamyl alcohol (2.68 g, 20 mmol), *p*-toluenesulfonylacetic acid (4.29 g, 20.0 mmol) and *N,N'*-diisopropylcarbodiimide (3.13 ml, 20 mmol) were employed in general procedure 1. Chromatography (1:99 Et_2O:CH_2Cl_2) gave **1c** (4.72 g, 71%) as a waxy white solid; m. pt. 42-44 °C; R_f 0.51 (5:95 Et_2O:CH_2Cl_2); ν_{max} (film) 3028, 2944, 1741, 1597, 1495, 1448, 1400, 1379, 1327, 1275, 1151, 1086, 968, 912, 814, 737, 694, 648 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 2.35 (s, 3H, Ts-CH_3), 4.17 (s, 2H, -SO_2-CH_2-), 4.72 (d, $^3J_{H,H}$ = 6.5 Hz, 2H, -O-CH_2-), 6.12 (dt, $^3J_{H,H}$ = 16.0, 6.5 Hz, 1H, Ph-CH=C*H*-), 6.59 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, Ph-CH=), 7.26-7.35 (m, 7H, other Ar-H), 7.82 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 21.7 (Ts-CH_3), 61.1 (-SO_2-CH_2-), 66.7 (-O-CH_2-), [121.7, 126.7, 128.4, 128.6, 128.7, 129.9 and 135.3] (3°), [135.6, 135.9 and 145.4] (4°), 162.4 (C=O); *m/z* (CI) 678 $[2M+NH_4]^+$, 464, 348 $[M+NH_4]^+$, 233, 188, 134 $[C_9H_{10}O]^+$, 117 $[C_9H_9]^+$, 64 (Found: $[M+NH_4]^+$, 348.1273 $C_{18}H_{18}O_4S$ requires $[M+NH_4]^+$, 348.1270)

(*E*)-Pent-2-enyl (toluene-4-sulfonyl)acetate (1d): (*E*)-2-penten-1-ol (431 mg, 5.0 mmol), *p*-toluenesulfonylacetic acid (1.07 g, 5.0 mmol) and *N,N'*-diisopropylcarbodiimide (0.79 ml, 5.0 mmol) in CH_2Cl_2 (20 ml) were employed in general procedure 1. Chromatography (10:90 EtOAc:petrol) gave **1d** (1.29 g, 91%) as a colourless oil; R_f 0.21 (10:90 EtOAc:petrol); ν_{max} (film) 2964, 2875, 1741, 1597, 1456, 1400, 1381, 1329, 1277, 1153, 1086, 1018, 970, 814, 727, 646 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 0.99 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, -CH_2-C*H*$_3$), 2.01-2.09 (m, 2H, -C*H*$_2$-CH_3), 2.45 (s, 3H, Ts-CH_3), 4.11 (s, 2H, -SO_2-CH_2-), 4.51 (d, $^3J_{H,H}$ = 6.5 Hz, 2H, -O-CH_2-), 5.38-5.48 (m, 1H, -O-CH_2-C*H*=), 5.74-5.81 (m, 1H, =C*H*-CH_2-CH_3), 7.36 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-SO_2-Ar) 7.81 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 13.0 (=CH-CH_2-*C*H_3), 21.7 (Ts-CH_3), 25.2 (-*C*H_2-CH_3), 61.1, 67.0, 121.6,

128.6, 129.8, 135.8, 139.3, 145.4, 162.3 (C=O); *m/z* (CI) 300 $[M+NH_4]^+$, 232, 188 (Found: $[M+NH_4]^+$, 300.1260. $C_{14}H_{18}O_4S$ requires $[M+NH_4]^+$ 300.1270) (Found: C, 59.35; H, 6.29. $C_{14}H_{18}O_4S$ requires C, 59.55; H, 6.43%).

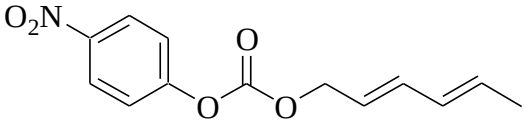
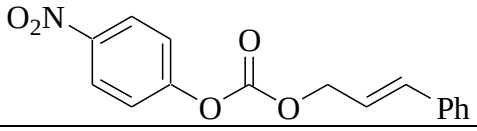
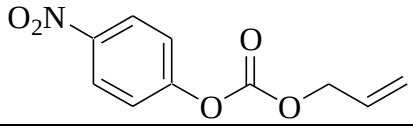
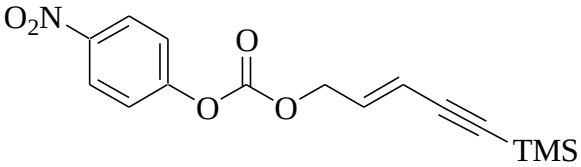
Allyl (toluene-4-sulfonyl)acetate (1e): Allyl alcohol (1.36 ml, 20 mmol), *p*-toluenesulfonylacetic acid (4.29 g, 20 mmol) and *N,N'*-diisopropylcarbodiimide (3.13 ml, 20 mmol) were employed in general procedure 1. Chromatography (35:65 EtOAc:petrol) gave **1e** (4.67 g, 92%) as a white solid; m. pt. 41 °C; R_f 0.49 (50:50 EtOAc:petrol); ν_{max} (film) 3005, 2947, 1739, 1649, 1597, 1495, 1450, 1400, 1361, 1327, 1292, 1151, 1086, 989, 935, 814, 729, 646 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 2.44 (s, 3H, Ts-CH_3), 4.12 (s, 2H, -SO_2-CH_2-), 4.56 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, -O-CH_2-), 5.20-5.30 (m, 2H, -CH=CH_2), 5.73-5.83 (m, 1H, -C*H*=CH_2), 7.35 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-SO_2-Ar), 7.80 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 21.7 (Ts-CH_3), 61.0 (-SO_2-CH_2-), 66.7 (-O-CH_2-), [119.4, 128.6, 129.9 and 130.9] (3°), [135.8 and 145.5] (4°), 162.2 (C=O); *m/z* (CI) 272 $[M+NH_4]^+$, 255 $[MH]^+$, 174, 155, 139, 108, 93, 91, 58 (Found: $[M+NH_4]^+$, 272.0969. $C_{12}H_{14}O_4S$ requires $[M+NH_4]^+$, 272.0957) (Found: C, 56.63; H, 5.81. $C_{12}H_{14}O_4S$ requires C, 56.68; H, 5.55%).

(E)-4-Nitrocinnamyl (toluene-4-sulfonyl)acetate (1f): *p*-Nitrocinnamyl alcohol (448 mg, 2.50 mmol), *p*-toluenesulfonylacetic acid (536 mg, 2.50 mmol) and *N,N'*-diisopropylcarbodiimide (0.39 ml, 2.50 mmol, 1.0 equiv) were employed in general procedure 1. Chromatography (40:60 EtOAc:petrol) gave **1f** (884 mg, 94%) as a pale yellow solid; m. pt. 90-91 °C; R_f 0.44 (50:50 EtOAc:petrol); ν_{max} (film) 3006, 2945, 1743, 1597, 1516, 1450, 1344, 1327, 1275, 1151, 1111, 1086, 972, 862, 816, 741, 644 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 2.41 (s, 3H, Ts-CH_3), 4.19 (s, 2H, -SO_2-CH_2-), 4.81 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, -O-CH_2-), 6.35 (dt, $^3J_{H,H}$ = 16.0, 5.5 Hz, 1H, Ar-CH=C*H*-), 6.71 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, Ar-CH=), 7.34 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-SO_2-Ar), 7.51 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *m*-NO_2-Ar), 7.82 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar) 8.19 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *o*-NO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 21.7 (Ts-CH_3), 61.0 (Ts-CH_2-), 65.8 (-O-CH_2-), [124.1, 126.7, 127.3, 128.6, 129.9 and 132.0] (3°), [135.7, 142.3, 145.6 and 147.3] (4°), 162.2 (C=O); *m/z* (CI) 393 $[M+NH_4]^+$, 321, 222, 205, 188, 134, 52 (Found: $[M+NH_4]^+$, 393.1122 $C_{18}H_{17}NO_6S$ requires $[M+NH_4]^+$,

393.1120) (Found: C, 57.76; H, 4.56; N, 3.85. $C_{18}H_{17}NO_6S$ requires C, 57.59; H, 4.56; N, 3.73%)

(*E*)-5-(Trimethylsilyl)pent-2-en-4-ynyl (toluene-4-sulfonyl)acetate (1g): 5-(Trimethylsilyl)pent-2-en-4-yn-1-ol (2.31 g, 15.0 mmol), *p*-toluenesulfonylacetic acid (3.21 g, 15.0 mmol) and *N,N'*-diisopropylcarbodiimide (2.35 ml, 15.0 mmol) were employed in general procedure 1. Chromatography (30:70 EtOAc:petrol) gave **1g** (3.40 g, 65%) as a pale yellow solid. A small portion was recrystallised from EtOAc/hexanes to give a white crystalline solid; m. pt. 78ºC; R_f 0.57 (50:50 EtOAc:petrol); ν_{max} (film) 3003, 2958, 2900, 2179, 2135, 1745, 1597, 1402, 1329, 1269, 1252, 1151, 1086, 955, 845, 760, 727, 644 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 0.12 (s, 9H, -Si$(CH_3)_3$), 2.36 (s, 3H, Ts-CH_3), 4.07 (s, 2H, -SO_2-CH_2-), 4.47 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, -O-CH_2-), 5.53 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, -O-CH_2-CH=C*H*-), 5.91 (dt, $^3J_{H,H}$ = 16.0, 6.0 Hz, 1H, -O-CH_2-C*H*=), 7.28 (d, $^3J_{H,H}$ = 8.0 Hz, d, *m*-SO_2Ar), 7.71 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = -0.2 (-Si$(CH_3)_3$), 21.7 (Ts-CH_3), 60.8 (-SO_2-CH_2-), 65.1 (-O-CH_2-), [96.6 and 102.3] (4°), [114.0, 128.5 and 129.9] (3°), 135.6 (4°), 136.0 (3°), 145.4 (4°), 162.0 (C=O); *m/z* (CI) 368 $[M+NH_4]^+$, 339, 214, 188, 154, 90 (Found: $[M+NH_4]^+$, 368.1344. $C_{17}H_{22}O_4SSi$ requires $[M+NH_4]^+$, 368.1352) (Found: C, 57.94; H, 6.25. $C_{17}H_{22}O_4SSi$ requires C, 58.25; H, 6.33%).

Allyl Carbonates **7**

Carbonate (*yield)*	Structure
7a (*76%*)	
7b (*86%*)	
7c (*91%*)	
7d (*75%*)	

General procedure (2) for the synthesis of (*p*-nitrophenyl) allyl carbonates (7a-e)
To *desired 3-substituted allyl alcohol* (1.0 equiv) and *p*-nitrophenyl chloroformate (1.1 equiv) CH_2Cl_2 (0.2 M). under N_2 at -10 °C was added dropwise triethylamine (2.0 equiv). The reaction mixture was stirred at -10 °C for 30 min, then at rt for 16 h. The reaction mixture was partitioned between EtOAc (15 ml $mmol^{-1}$) and saturated $NH_4Cl_{(aq)}$ (7.5 ml $mmol^{-1}$). The organic phase was washed with saturated $NH_4Cl_{(aq)}$ (2 × 7.5 ml $mmol^{-1}$), dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography (EtOAc-petrol) or recrystallisation afforded the *p*-nitrophenyl allyl carbonates in good yield.

(2*E*,4*E*)-Hexa-2,4-dienyl 4-nitrophenyl carbonate (7a): *p*-Nitrophenyl chloroformate (4.44 g, 22 mmol), (2*E*,4*E*)-hexa-2,4-dien-1-yl alcohol (1.96 g, 20 mmol) and triethylamine (5.58 ml, 40 mmol) were employed in general procedure 2. Chromatography (15:85 EtOAc:petrol) gave **7a** (3.99 g, 76%) as a white solid; m. pt. 92 °C; R_f 0.48 (20:80 EtOAc:petrol); ν_{max} (film) 3116, 3086, 3005, 2943, 1749, 1660, 1531,

1493, 1350, 1300, 1273, 1221, 1107, 997, 980, 939, 858, 777, 723, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 1.81 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, =CH-C*H*$_3$), 4.79 (d, $^3J_{H,H}$ = 7.0 Hz, 2H, -O-CH_2-), 5.66-5.92 (m, 2H, -O-CH_2-C*H*= and =C*H*-CH_3), 6.07-6.15 (m, 1H, -O-CH_2-CH=CH-C*H*=), 6.38 (dd, $^3J_{H,H}$ = 15.0, 10.5 Hz, 1H, -O-CH_2-CH=C*H*-), 7.40 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, *m*-NO_2-Ar), 8.31 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, *o*-NO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 18.2 (-CH_3), 69.9 (-O-CH_2-), [121.6, 121.8, 125.3, 130.1, 132.8 and 137.0] (3°), [145.4, 152.4 and 155.6] (4°); *m/z* (CI) 281 $[M+NH_4]^+$, 252, 234, 217, 110 (Found: $[M+NH_4]^+$, 281.1137. $C_{13}H_{13}NO_5$ requires $[M+NH_4]^+$, 281.1137) (Found: C, 59.10; H, 4.79; N, 5.33. $C_{13}H_{13}NO_5$ requires C, 59.31; H, 4.94; N, 5.32%).

Cinnamyl *p*-nitrophenyl carbonate (7b): *p*-Nitrophenyl chloroformate (8.87 g, 44 mmol), cinnamyl alcohol (5.37 g, 40 mmol), and triethylamine (11.15 ml, 80 mmol) were employed in general procedure 2. Recrystallisation from 20% TBME-petrol gave **7b** (10.27 g, 86%) as a white crystalline solid; m. pt. 78 °C (lit.[22] 77 °C); R_f 0.28 (20:80 EtOAc:petrol); ν_{max} (film) 3116, 3084, 3060, 3028, 2954, 1763, 1616, 1593, 1523, 1493, 1448, 1348, 1255, 1211, 1109, 968, 858, 746, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 4.96 (d, $^3J_{H,H}$ = 6.5 Hz, 2H, -CH_2-O-), 6.38 (dt, $^3J_{H,H}$ = 16.0, 6.5 Hz, 1H, Ph-CH=C*H*-), 6.80 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, Ph-CH=), 7.28-7.47 (m, 7H, other Ar-H), 8.31 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, *o*-NO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 155.6 (4° -NO_2Ar), 152.4 (-OCO_2-), 145.4 (4° -NO_2Ar), 136.3, 135.7 (4° Ph), 128.8, 128.6, 126.8, 125.4, 121.9, 121.2, 69.9 (-CH_2-O-); *m/z* (CI) 317 $[M+NH_4]^+$, 273, 252, 226, 157, 151, 134 $[C_9H_{10}O]^+$, 117 $[C_9H_9]^+$ (Found: $[M+NH_4]^+$, 317.1147. $C_{16}H_{13}NO_5$ requires $[M+NH_4]^+$, 317.1137) (Found: C, 64.34; H, 4.27; N, 4.58. $C_{16}H_{13}NO_5$ requires C, 64.21; H, 4.38; N, 4.68%).

Allyl *p*-nitrophenyl carbonate (7c): *p*-Nitrophenyl chloroformate (4.44 g, 22 mmol), allyl alcohol (1.36 ml, 20 mmol) and triethylamine (11.1 ml, 80 mmol) were employed in general procedure 2. Chromatography (15:85 EtOAc-petrol) afforded **7c** (4.04 g, 91%) as an off-white solid; m. pt. 49 °C; R_f 0.48 (20:80 EtOAc:petrol); ν_{max} (film) 3120, 3086, 2954, 2854, 1753, 1614, 1595, 1518, 1489, 1361, 1300, 1265, 1225, 1163, 1105, 1051, 993, 939, 856, 775, 727, 677 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 4.80 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, -O-CH_2-), 5.37-5.51 (m, 2H, -CH=C*H*$_2$), 5.96-6.09 (m, 1H, -C*H*=CH_2), 7.41 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, *m*-NO_2-Ar), 8.30 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, *o*-NO_2-Ar), in agreement with previously reported values[23]; ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ =

69.8 (-O-CH_2-), 120.2 (=CH_2), [121.8, 125.3 and 130.6] (3°), [145.4, 152.3 and 155.5] (4°); *m/z* (CI) 241 $[M+NH_4]^+$, 211, 194, 157, 148, 110, 108 (Found: $[M+NH_4]^+$, 241.0826. $C_{10}H_9NO_5$ requires $[M+NH_4]^+$, 241.0824) (Found: C, 53.73; H, 3.93; N, 6.19. $C_{10}H_9NO_5$ requires C, 53.82; H, 4.06; N, 6.28%).

***p*-Nitrophenyl (*E*)-5-trimethylsilanylpent-2-en-4-ynyl carbonate (7d):** *p*-Nitrophenyl chloroformate (2.22 g, 11 mmol), (*E*)-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (1.54 g, 10 mmol) and triethylamine (2.79 ml, 20 mmol) were employed in general procedure 2. Chromatography (15:85 EtOAc:petrol) gave **7d** (2.40 g, 75%) as a colourless oil; R_f 0.52 (20:80 EtOAc:petrol); ν_{max} (film) 3118, 3087, 2960, 2177, 2137, 1768, 1616, 1595, 1527, 1493, 1350, 1252, 1215, 1165, 1084, 953, 920, 847, 760, cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 0.21 (s, 9H, -Si$(CH_3)_3$), 4.80 (d, $^3J_{H,H}$ = 6.5 Hz, 2H, -O-CH_2-), 5.90 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, -O-CH_2-CH=C*H*-), 6.28 (dt, $^3J_{H,H}$ = 16.0, 6.5 Hz, 1H, -O-CH_2-C*H*=), 7.39 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, *m*-NO_2-Ar), 8.29 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, *o*-NO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = -0.2 (-Si$(CH_3)_3$), 68.4 (-O-CH_2-), 97.6 (-C≡*C*-Si$(CH_3)_3$), 101.8 (-*C*≡C-Si$(CH_3)_3$), 115.4, 121.8, 125.4, 135.3, 145.5, 152.2, 155.4; *m/z* (CI) 337 $[M+NH_4]^+$, 307, 229, 171, 154, 137, 90, 76, 52 (Found: $[M+NH_4]^+$, 337.1219. $C_{15}H_{17}NO_5Si$ requires $[M+NH_4]^+$, 337.1220) (Found: C, 56.69; H, 5.27; N, 4.36. $C_{15}H_{17}NO_5Si$ requires C, 56.41; H, 5.36; N, 4.39%).

Preparation of Allyl alcohols.

- Allyl alcohol was purchased from Aldrich Chemical Co. Inc. and distilled prior to use.

- Cinnamyl alcohol and *p*-nitrocinnamyl alcohol were purchased from Lancaster Synthesis Ltd.

- Pent-2-enyl alcohol and (2*E*,4*E*)-hexa-2,4-dien-1-yl alcohol were purchased from Aldrich Chemical Co. Inc.

- *p*-Methoxycinnamyl alcohol was prepared in accordance with previously reported procedures, in two steps from *p*-anisaldehyde, purchased from Aldrich Chemical Co. Inc.

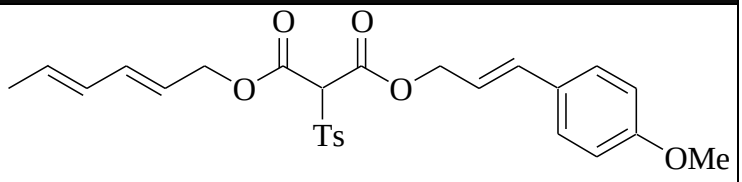
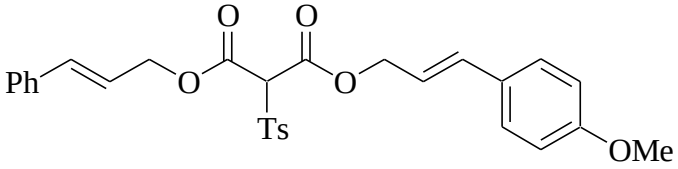
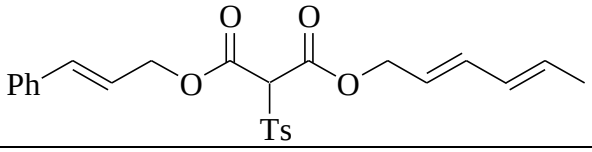
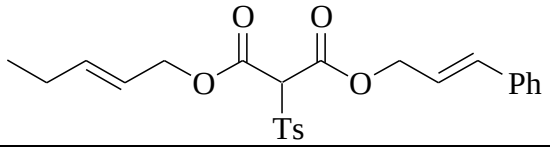
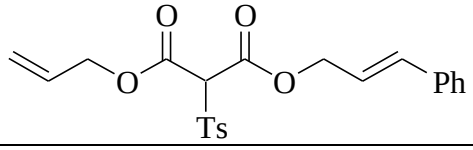
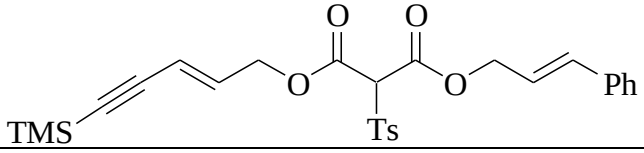
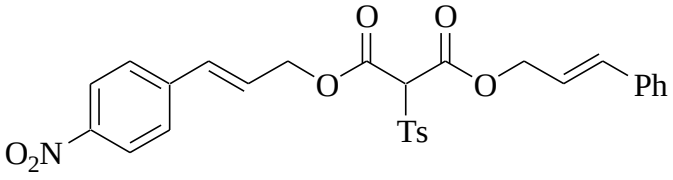
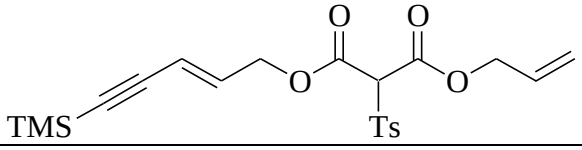
Step 1: Ethyl *p*-methoxycinnamate: To a suspension of sodium hydride (720 mg, 30 mmol, 1.0 equiv) in THF (60 ml) at 0 °C was added triethylphosphonoacetate (7.06 g, 31.5 mmol, 1.05 equiv, solution in THF, 30 ml) dropwise *via* a cannula. The reaction mixture was stirred for 30 min at 0 °C, then *p*-anisaldehyde 61 (3.64 ml, 30 mmol, 1.0 equiv, solution in THF, 30 ml) was introduced dropwise *via* a cannula *with vigorous stirring*. The reaction mixture was allowed to warm to rt and stirred for 41 h before dilution with EtOAc (100 ml). The organic phase was washed with saturated $NH_4Cl_{(aq)}$ (2 × 75ml), dried (Na_2SO_4), concentrated under reduced pressure and purified by chromatography (5:95 EtOAc:petrol) to give ethyl *p*-methoxycinnamate (4.78 g, 77%) as a white crystalline solid; R_f 0.35 (20:80 EtOAc:petrol); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 1.34 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, -O-CH_2-C*H*$_3$), 3.84 (3H, s, Ar-O-CH_3), 4.26 (q, $^3J_{H,H}$ = 7.0 Hz, 2H, -O-C*H*$_2$-CH_3), 6.32 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, Ar-CH=C*H*-), 6.91 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *o*-MeO-Ar), 7.48 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *m*-MeO-Ar), 7.65 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, Ar-CH=); data in agreement with those previously reported.[24]

Step 2: *p*-Methoxycinnamyl alcohol: To a solution of ethyl *p*-methoxycinnamate (4.78 g, 23.2 mmol, 1.0 equiv) in CH_2Cl_2 (100 ml) at -78 °C was added dropwise over 5min di-*iso*butyl aluminium hydride (1.0M in CH_2Cl_2, 83.5 ml, 83.5 mmol, 3.6 equiv). The reaction mixture was stirred at -78 °C for 30 min then allowed to warm to rt over 45min. Dropwise addition of EtOAc (10 ml) to the reaction mixture was followed by the reaction mixture being *slowly* poured into a solution of 100ml saturated aqueous sodium potassium tartrate solution and 100 ml H_2O *with vigorous stirring*. The reaction mixture was stirred at rt for 14 h then the organic phase was washed with saturated $NaCl_{(aq)}$ (2 × 100ml), dried (Na_2SO_4), concentrated under reduced pressure and purified by chromatography (20:80 to 50:50 EtOAc:petrol) to give *p-m*ethoxycinnamyl alcohol (3.27 g, 86%) as a white crystalline solid; R_f 0.09 (20:80 EtOAc:petrol); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 1.63 (br s, 1H, -OH), 3.83 (s, 3H, Ar-O-CH_3), 4.31 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, -CH_2-O-), 6.21-6.30 (1H, m, Ar-CH=C*H*-), 6.57 (1H, d, $^3J_{H,H}$ = 16.0 Hz, Ar-CH=), 6.88 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-MeO-Ar), 7.34 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-MeO-Ar); data in agreement with those previously reported.[25]

- (*E*)-5-(trimethylsilyl)pent-2-en-4-yn-1-ol was prepared in one step in accordance with a previously reported procedure from pent-2-en-4-yn-1-ol, purchased as an unspecified mixture of (*E*) and (*Z*) isomers from Lancaster Synthesis Ltd.

(*E*)-5-Trimethylsilyl-pent-2-en-4-yn-1-ol: To a solution of pent-2-en-4-yn-1-ol (mixture of *E/Z* isomers, 4.11 g, 50 mmol, 1.0 equiv) in THF (85 ml) at -78 °C was added *n*-butyllithium (2.48M; in THF, 40.3 ml, 100 mmol, 2.0 equiv). A green precipitate formed; to this was added chlorotrimethylsilane (10.86 g, 100 mmol, 2.0 equiv). The reaction mixture was stirred at -78 °C for 30 min then allowed to warm to rt over 30 min. The reaction mixture was poured over 2M $HCl_{(aq)}$ (200 ml), then extracted with Et_2O (100 ml). The organic phase was washed with 2M $HCl_{(aq)}$ (200 ml), dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography (15:85 EtOAc:petrol) yielded (*E*)-5-trimethylsilanyl-pent-2-en-4-yn-1-ol (983 mg, 66%) as a colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 0.20 (s, 9H, -Si(CH_3)$_3$), 1.80 (br s, 1H, -OH), 4.20 (d, $^3J_{H,H}$ = 5.0 Hz, 2H, HO-CH_2-), 5.78 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, HO-CH_2CH=C*H*-), 6.31 (dt, $^3J_{H,H}$ = 16.0, 5.0 Hz, 1H, HO-CH_2-C*H*=); data in agreement with those previously reported.[26]

Synthesis of Tosylmalonates **5**

Tosylmalonate (*yield)*	Structure
5a (*16%*)	
5b (39%)	
5c (*30%*)	
5d (*56%*)	
5e (*46%*)	
5f (*28%*)	
5g (23%)	
5h (*17%*)	

General procedure (3) for the synthesis of 2-(Toluene-4-sulfonyl)malonic acid bis(allyl) esters (5a-g)

To NaH (2.0 equiv) under N_2 at 0°C was added via cannula a solution of *desired tosyl monoester* **1** (1.0 equiv) in DMF (5 ml mol^{-1}, dry), resulting in effervescence. The reaction mixture was stirred for 15 min, then a solution of *desired* p-*nitrocinnamyl allyl carbonate* **7** (1.0 equiv) in DMF (5 ml mol^{-1}, dry) was introduced via cannula. The yellow reaction mixture was stirred at 0°C for 15 min, then at rt for 16 h. The reaction mixture was then diluted with EtOAc (10 ml $mmol^{-1}$) and washed with H_2O (2 × 10 ml $mmol^{-1}$). The organic phase was dried over Na_2SO_4, concentrated under reduced pressure and purified by chromatography (EtOAc-PhMe or Et_2O-CH_2Cl_2, with NEt_3 or AcOH additive as necessary) to give the desired 2-(toluene-4-sulfonyl)malonic acid bis(allyl) ester **5.**

(±)-((2*E*,4*E*)-Hexa-2,4-dienyl)(4-methoxycinnamyl)-2-(toluene-4-sulfonyl)malonate (5a): sodium hydride (254 mg, 6.34 mmol), (*E*)-4-methoxycinnamyl (toluene-4-sulfonyl)acetate **1a** (1.141 g, 3.17 mmol) and *p*-nitrophenyl (2*E*,4*E*)-hexa-2,4-dien-1-yl carbonate **7a** (834 mg, 3.17 mmol) were employed in general procedure 3, *with the following additions*: The ethyl acetate solution of the crude product was concentrated under reduced pressure *without heating.* Chromatography (70:927:3 EtOAc:PhMe:NEt_3) gave an inseparable mixture of the desired product and unreacted **1a**. This mixture was dissolved in DMF (15 ml, dry), to which was added at 0 °C DBU (1.59 ml, 15.9 mmol, 5.0 equiv) and sodium iodoacetate (3.30 g, 15.9 mmol, 5.0 equiv). The reaction mixture was allowed to warm to rt with stirring over 2 h, then diluted with CH_2Cl_2 (40 ml). The resultant white suspension was washed with H_2O (40 ml), then the aqueous layer was backwashed with a small portion of CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure *without heating* and purified by chromatography (200:800:3 EtOAc:hexane:NEt_3) to give pure **5a** (249 mg, 16%) as a colourless oil; R_f 0.18 (20:80 EtOAc:hexane); ν_{max} (film) 2924, 2853, 1738, 1606, 1612, 1444, 1378, 1333, 1247, 1175, 1148, 1082, 1031, 991, 968, 841, 814, 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.75 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, =CH-C*H*$_3$), 2.38 (s, 3H, Ts-CH_3), 3.81 (s, 3H, -OCH_3), 4.65 (d, $^3J_{H,H}$ = 7.0 Hz, 2H, -CH_2-O-), 4.77 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, -CH_2-O-), 4.98 (1H, s, -OCO-CH(Ts)-COO-), 5.50 (dt, $^3J_{H,H}$ = 14.5, 7.0 Hz, 1H=C*H*-CH_3), 5.70-5.78 (m, 1H, -O-CH_2-C*H*=CH-CH=), 5.94-6.01 (1H, m, -O-CH_2-CH=CH-C*H*=), 6.03 (dt, $^3J_{H,H}$ = 16.0, 6.5 Hz, 1H, p-MeO-C_6H_4-CH=C*H*-), 6.21 (dd, $^3J_{H,H}$ = 15.0, 10.5 Hz, 1H, -O-CH_2-CH=C*H*-CH=), 6.58 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, MeO-C_6H_4-C*H*=), 6.86 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, *o*-MeO-Ar), 7.25-7.31 (m, 4H, other Ar-H), 7.83 (d, $^3J_{H,H}$ =

8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 18.1 (=CH-*C*H_3), 21.7 (Ts-CH_3), 55.3 (-OCH_3), [67.4 and 67.7] (2 × -CH_2-O-), 74.7 (-OCO-*C*H(Ts)-COO-), [114.1, 119.0, 121.8 and 128.0] (3°), 128.6 (4°), [129.4, 2 × 130.2 and 132.2] (3°), 134.2 (4°), [135.5 and 136.3] (3°), 145.9 (4° SO_2-Ar), 159.8 (4° MeO-Ar), 160.8 (2 × C=O); *m/z* (-ve ESI) 483 $[M-H]^-$, 457 (Found: 483.1467. $C_{26}H_{28}O_7S$ requires $[M-H]^-$ 483.1483) (Found: C, 64.37; H, 6.04. $C_{26}H_{28}O_7S$ requires C, 64.47; H, 5.83%).

(±)-(Cinnamyl)(4-methoxycinnamyl)-2-(toluene-4-sulfonyl)malonate (5b): sodium hydride (480 mg, 20 mmol), (*E*)-4-methoxycinnamyl (toluene-4-sulfonyl)acetate **1a** (3.60 g, 10 mmol) and cinnamyl *p*-nitrophenyl carbonate **7b** (2.99 g, 10 mmol) were employed in general procedure 3. Chromatography (4:96 EtOAc:PhMe) gave **5b** (2.03 g, 39%) as a pale yellow oil; R_f 0.62 (50:50 EtOAc:petrol); ν_{max} (film) 3028, 2954, 2839, 1741, 1606, 1512, 1448, 1377, 1334, 1252, 1176, 1149, 1082, 1032, 970, 843, 814, 746, 706, 694, 671 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 2.35 (s, 3H, Ts-CH_3), 3.81 (3H, s, Ar-O-CH_3), 4.79-4.84 (m, 4H, -O-CH_2-), 5.04 (s, 1H, -OCO-CH(Ts)-COO-), [6.04 and 6.17] (each dt, $^3J_{H,H}$ = 16.0, 6.5 Hz, each 1H, Ph-CH=C*H*- and MeO-Ar-CH=C*H*-), [6.59 and 6.64] (each d, $^3J_{H,H}$ = 16.0 Hz, each 1H, Ph-CH= and MeO-Ar-C*H*=-), 6.84 (dt, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 2.5 Hz, 2H, *o*-MeO-Ar), 7.21-7.36 (m, 9H, other Ar-H), 7.85 (dt, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 21.7 (Ts-CH_3), 55.3 (Ar-O-CH_3), [67.5 and 67.9] (2× -O-CH_2-), 74.6 (-OCO-*C*H(Ts)-COO-), 114.1, 118.9, 121.3, 126.8, 128.1, 128.4, 128.6, 128.7, 129.5 (4° -MeO-Ar), 130.3, 134.1, 2 × 135.6, 135.8, 146.0 (4° -SO_2-Ar), 159.9 (4° -MeO-Ar), 160.8 (2× C=O); *m/z* (FAB) 521 $[MH]^+$, 520, 430, 338, 147 $[C_{10}H_{11}O]^+$, 117 $[C_9H_9]^+$, 109 (Found: $[M]^+$, 520.1570. $C_{29}H_{28}O_7S$ requires $[M]^+$, 520.1556) (Found: C, 66.85; H, 5.60. $C_{29}H_{28}O_7S$ requires C, 66.91; H, 5.42%).

(±)-(Cinnamyl)((2*E*,4*E*)-hexa-2,4-dienyl)-2-(toluene-4-sulfonyl)malonate (5c): Sodium hydride (480 mg, 20 mmol), (2*E*,4*E*)-Hexa-2,4-dienyl (toluene-4-sulfonyl)acetate **1b** (2.94 g, 10 mmol) and cinnamyl *p*-nitrophenyl carbonate **7b** (2.99 g, 10 mmol, 1.0 equiv) were employed in general procedure 3. Chromatography (10:987:3 Et_2O:CH_2Cl_2:AcOH, then 4:96 EtOAc:PhMe) gave **5c** (1.36 g, 30%) as a yellow oil; R_f 0.18 (20% EtOAc-petrol); ν_{max} (film) 3026, 2937, 1741, 1660, 1597, 1495, 1448, 1379, 1336, 1271, 1151, 1082, 991, 970, 814, 746, 706, 692, 673 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 1.77 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, C*H*$_3$-CH=), 2.40 (s, 3H, Ts-CH_3), [4.68

and 4.84] (each d, $^{3}J_{H,H}$ = 6.5 Hz, each 2H, 2 × -CH_2-O-), 5.03 (s, 1H, -CH(Ts)-COO-), 5.49-5.58 (m, 1H, CH_3-C*H*=), 5.73-5.83 (m, 1H, CH_3-CH=CH-CH=C*H*-), 5.96-6.05 (m, 1H, CH_3-CH=C*H*-), 6.14-6.29 (m, 2H, Ph-CH=C*H*- and CH_3-CH=CH-C*H*=), 6.66 (d, $^{3}J_{H,H}$ = 16.0 Hz, 1H, Ph-CH=), 7.28-7.39 (m, 7H, other Ar-H), 7.86 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 18.2 (=CH-*C*H_3), 21.8 (Ts-CH_3), [67.4 and 67.5] (2 × -O-CH_2-), 74.6 (-*C*H(Ts)-COO-), 121.2, 121.8, 126.8, 128.4, 128.7, 129.5, 130.2, 130.3, 132.3, 134.1 (4° Ph), 135.6, 135.8, 136.4, (4° -SO_2Ar), 146.0 (4° -SO_2Ar), 2 × 160.8 (2 × C=O); *m/z* (CI) 472 $[M+NH_4]^+$, 436, 348, 312, 297, 231, 188, 134 $[C_9H_{10}O]^+$, 117 $[C_9H_9]^+$, 98 $[C_6H_{10}O]^+$, 81 $[C_6H_9]^+$ (Found: 472.1777. $[M+NH_4]^+$, $C_{25}H_{26}O_6S$ requires $[M+NH_4]^+$, 472.1794).

(±)-(Cinnamyl)((2*E*)-pent-2-enyl)-2-(toluene-4-sulfonyl)malonate (5d): Sodium hydride (48 mg, 2.0 mmol), (*E*)-pent-2-enyl (toluene-4-sulfonyl)acetate **1d** (282 mg, 1.0 mmol) and cinnamyl *p*-nitrophenyl carbonate **7b** (299 mg, 1.0 mmol, 1.0 equiv) were employed in general procedure 3. Chromatography (10:987:3 Et_2O:CH_2Cl_2:AcOH) gave **5d** (250 mg, 56%) as a yellow oil; R_f 0.62 (5:95 Et_2O:CH_2Cl_2); ν_{max} (film) 2962, 2933, 1741, 1597, 1495, 1450, 1377, 1336, 1261, 1149, 1082, 968, 814, 744, 706, 694, 669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 0.99 (t, $^{3}J_{H,H}$ = 7.0 Hz, 3H, -CH_2-C*H*$_3$), 2.01-2.10 (m, 2H, -C*H*$_2$-CH_3), 2.40 (s, 3H, Ts-CH_3), 4.63 (d, $^{3}J_{H,H}$ = 6.5 Hz, 2H, -C*H*$_2$-CH=CH-CH_2-CH_3), 4.84 (d, $^{3}J_{H,H}$ = 6.5 Hz, 2H, Ph-CH=CH-C*H*$_2$-), 5.04 (s, 1H, -CH(Ts)-), 5.50 (dt, $^{3}J_{H,H}$ = 15.5, 6.0 Hz, 1H, -O-CH_2-C*H*=CH-CH_2-), 5.84 (dt, $^{3}J_{H,H}$ = 15.5, 6.0 Hz, 1H, -O-CH_2-CH=C*H*-CH_2-), 6.19 (dt, $^{3}J_{H,H}$ = 16.0, 6.5 Hz, 1H, Ph-CH=C*H*-), 6.57 (1H, d, $^{3}J_{H,H}$ = 16.0 Hz, Ph-CH=), 7.19-7.29 (m, 7H, other Ar-H), 7.78 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 13.0 (-CH_2-*C*H_3), 21.8 (Ts-CH_3), 25.3 (-*C*H_2-CH_3), 67.5 (Ph-CH=CH-*C*H_2-), 67.8 (-O-*C*H_2-CH=CH-CH_2-), 74.6 (-CH(Ts)-), [121.2 and 121.3] (Ph-CH=*C*H- and -O-CH_2-*C*H=CH-CH_2), [126.8, 128.4 and 128.7] (3° Ph), 129.5 (3° SO_2-Ar), 130.3 (3° SO_2-Ar), 134.1 (4° SO_2-Ar), 135.6 (Ph-CH=), 135.8 (*i*-Ph), 139.7 (-O-CH_2-CH=*C*H-CH_2-), 146.0 (4° SO_2-Ar), [160.8 and 160.9] (2 × C=O); *m/z* (CI) 460 $[M+NH_4]^+$, 338, 300, 188, 174, 146, 134 $[C_9H_{10}O]^+$, 117 $[C_9H_9]^+$ (Found: $[M+NH_4]^+$, 460.1784 $C_{24}H_{26}O_6S$ requires $[M+NH_4]^+$, 460.1794) (Found: C, 65.31; H, 6.11. $C_{24}H_{26}O_6S$ requires C, 65.14; H, 5.92%).

(±)-(Allyl)(cinnamyl)-2-(toluene-4-sulfonyl)malonate (5e): Sodium hydride (480 mg, 20 mmol), allyl (toluene-4-sulfonyl)acetate **1e** (2.54 g, 10 mmol) and cinnamyl *p*-nitrophenyl carbonate **7b** (2.99 g, 10.0 mmol) were employed in general procedure 3. Chromatography (10:987:3 Et_2O:CH_2Cl_2:AcOH, then 3:97 EtOAc:PhMe) gave **5e** (1.89 g, 46%) as a colourless oil; R_f 0.34 (50:50 EtOAc:petrol); ν_{max} (film) 3058, 3027, 2946, 1743, 1596, 1494, 1449, 1336, 1276, 1151, 1084, 970, 939, 815, 747, 705, 694, 673 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 2.40 (s, 3H, Ts-CH_3), 4.69 (d, $^3J_{H,H}$ = 5.0 Hz, 2H, -C*H*$_2$-CH=CH_2), 4.84 (d, $^3J_{H,H}$ = 6.5 Hz, 2H, Ph-CH=CH-C*H*$_2$-), 5.05 (s, 1H, -CH(Ts)-), 5.24-5.38 (m, 2H, -CH=C*H*$_2$), 5.80-5.91 (m, 1H, -C*H*=CH_2), 6.19 (dt, $^3J_{H,H}$ = 16.0, 6.5 Hz, 1H, Ph-CH=C*H*-), 6.66 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, Ph-CH=), 7.28-7.40 (m, 7H, other Ar-H), 7.87 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 21.8 (Ts-CH_3), [67.4 and 67.5] (2× -O-CH_2-), 74.6 (-SO_2-CH<), 119.7, 121.3, 126.8, 128.5, 128.7, 129.6, 130.3, 130.5, 130.7, 134.1, 135.8, 146.1, [160.7 and 160.8] (2 × C=O); *m/z* (CI) 432 $[M+NH_4]^+$, 388, 356, 272, 202, 174, 134 $[C_9H_{10}O]^+$, 117 $[C_9H_9]^+$ (Found: $[M+NH_4]^+$, 432.1481. $C_{22}H_{22}O_6S$ requires $[M+NH_4]^+$, 432.1481) (Found: C, 63.78; H, 5.40. $C_{22}H_{22}O_6S$ requires C, 63.75; H, 5.35%).

(±)-(Cinnamyl)(5-trimethylsilanylpent-2-en-4-ynyl)-2-(toluene-4-sulfonyl)malonate (5f): Sodium hydride (48 mg, 2.00 mmol), (*E*)-5-(trimethylsilyl)pent-2-en-4-ynyl (toluene-4-sulfonyl)acetate **1g** (351 mg, 1.00 mmol) and cinnamyl *p*-nitrophenyl carbonate **7b** (299 mg, 1.00 mmol) were employed in general procedure 3. Chromatography (10:987:3 Et_2O:CH_2Cl_2:AcOH) gave **5f** (143 mg, 28%) as a yellow oil; R_f 0.71 (5:95 Et_2O:CH_2Cl_2); ν_{max} (film) 3028, 2958, 2179, 2135, 1745, 1597, 1495, 1448, 1377, 1336, 1252, 1151, 1084, 968, 847, 816, 760, 706, 694, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.22 (s, 9H, -Si(CH_3)$_3$), 2.41 (s, 3H, Ts-CH_3), 4.67 (ddd, $^3J_{H,H}$ = 14.0, 6.0 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, -C*H*H-CH=CH-C≡), 4.71 (ddd, $^3J_{H,H}$ = 14.0, 6.0 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, -CH*H*-CH=CH-C≡), 4.81 (ddd, $^3J_{H,H}$ = 12.5, 6.5 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, -C*H*H-CH=CH-Ph), 4.85 (ddd, $^3J_{H,H}$ = 12.5, 6.5 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, -CH*H*-CH=CH-Ph), 5.04 (s, 1H, -CH(Ts)-), 5.73 (dt, $^3J_{H,H}$ = 16.0 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, -CH=C*H*-C≡), 6.10 (dt, $^3J_{H,H}$ = 16.0, 6.0 Hz, 1H, -C*H*=CH-C≡), 6.18 (dt, $^3J_{H,H}$ = 16.0, 6.5 Hz, 1H, Ph-CH=C*H*-), 6.65 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, Ph-CH=), 7.26-7.40 (m, 7H, other Ar-H), 7.84 (dt, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = -0.2 (-Si(CH_3)$_3$), 21.8 (Ts-CH_3), 65.9 (-*C*H_2-CH=CH-C≡), 67.5 (-*C*H_2-CH=CH-Ph), 74.5 (-*C*H(Ts)-), 97.2 (-C≡*C*-Si(CH_3)$_3$), 102.0 (-*C*≡C-Si(CH_3)$_3$), 114.8

(-CH=*C*H-C≡), 121.2 (Ph-CH=*C*H-), [126.8, 128.5 and 128.7] (3° Ph), 129.6 (*m*-SO_2-Ar), 130.2 (*o*-SO_2-Ar), 134.0 (4° SO_2-Ar), 135.3 (-*C*H=CH-C≡), 135.8 (*i*-Ph), 135.8 (Ph-CH=), 146.2 (4° SO_2-Ar), [160.5 and 160.7] (2× C=O); *m/z* (-ve CI) 509 $[M-H]^-$, 375, 213, 169, 155, 138 (Found: C, 63.71; H, 6.16. $C_{27}H_{30}O_6SSi$ requires C, 63.50; H, 5.92%).

(±)-1-Cinnamyl 3-(*E*)-3-(4-nitrophenyl)allyl 2-(toluene-4-sulfonyl)malonate (5g) and (3*S,4*R**)-Cinnamyl 4-(4-nitrobenzyl)-2-oxo-3-(toluene-4-sulfonyl)tetrahydrofuran-3-carboxylate (11):** Sodium hydride (50 mg, 2.09 mmol), (*E*)-4-nitrocinnamyl (toluene-4-sulfonyl)acetate **1f** (783 mg, 2.09 mmol) and cinnamyl *p*-nitrophenyl carbonate **7b** (625 mg, 2.09 mmol) were employed in general procedure 3. Chromatography (10:990:3 Et_2O:CH_2Cl_2:AcOH) gave **11** (383 mg, 34%) as a pale yellow solid and **5g** (261 mg, 23%) as a yellow oil.

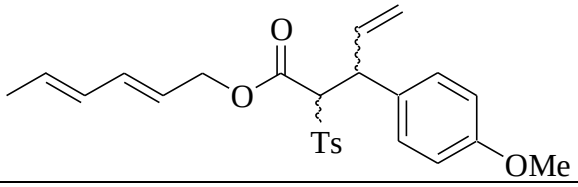
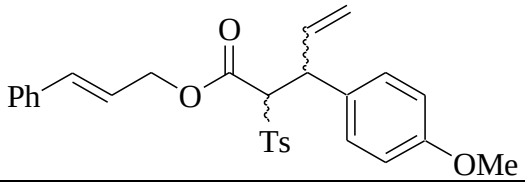
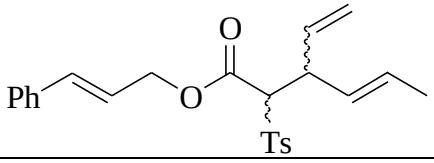
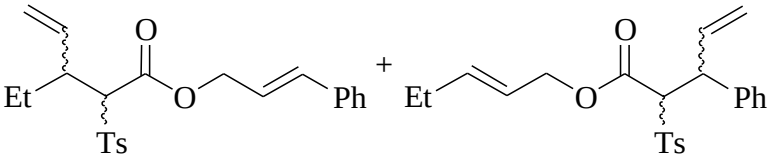
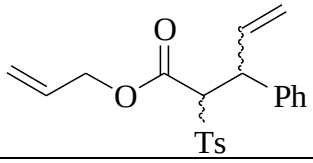
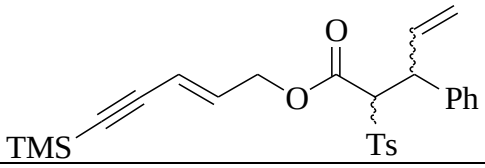
5g: R_f 0.63 (5:95 Et_2O:petrol); ν_{max} (film) 3113, 3059, 3028, 1743, 1657, 1597, 1516, 1495, 1448, 1377, 1342, 1149, 1082, 1016, 970, 912, 862, 816, 737, 706, 692, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ = 2.38 (s, 3H, Ts-CH_3), 4.82 (ddd, $^3J_{H,H}$ = 6.5, 2.5, 1.5 Hz, 2H, Ph-CH=CH-CH_2O-), 4.90 (d, $^3J_{H,H}$ = 6.0 Hz, 2H O_2N-C_6H_4-CH=CH-CH_2O-), 5.10 (s, 1H, -CH(Ts)-), 6.15 (dt, $^3J_{H,H}$ = 16.0, 6.5 Hz, 1H, Ph-CH=C*H*-), 6.36 (dt, $^3J_{H,H}$ = 16.0, 6.0 Hz, 1H, O_2N-C_6H_4-CH=C*H*-), 6.62 (dd, $^3J_{H,H}$ = 16.0 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H, Ph-CH=), 6.71 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, O_2N-C_6H_4-C*H*=), 7.26-7.34 (m, 7H, other Ar-H), 7.44 (dd, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, *m*-NO_2Ar), 7.86 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, *o*-SO_2Ar), 8.12 (dd, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, *o*-NO_2Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 21.8 (Ts-CH_3), 66.5 (O_2N-C_6H_4-CH=CH-*C*H_2O-), 67.6 (Ph-CH=CH-*C*H_2O-), 74.5 (-CH(Ts)-), 121.1 (Ph-CH=*C*H-), 124.0 (3° NO_2Ar), 126.2 (O_2N-C_6H_4-CH=*C*H-), 126.7 (3° Ph), 127.3 (3° NO_2Ar), [128.6, 128.7] (3° Ph), [129.6, 130.2] (3° SO_2Ar), 132.3 (O_2N-C_6H_4-*C*H=), 134.1 (4° SO_2Ar), 135.7 (4° Ph), 135.9 (Ph-CH=), 142.2 (4° NO_2Ar), 146.2 (4° SO_2Ar), 147.4 (4° NO_2-Ar), 160.7 (2× C=O); *m/z* (FAB) 536 $[M+H]^+$, 486, 391, 133, 117, 91, 77, 69, 57 (Found: C, 63.09; H, 4.95; N, 2.65. $C_{28}H_{25}NO_8S$ requires C, 62.79; H, 4.71; N, 2.62%).

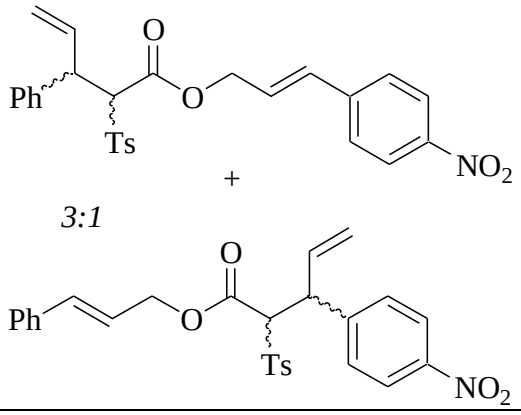
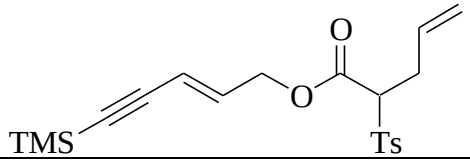
11: mp 192 °C; R_f 0.74 (5% Et_2O–CH_2Cl_2); ν_{max} (film) 3107, 3078, 3059, 3028, 1793, 1751, 1597, 1522, 1495, 1448, 1379, 1348, 1329, 1308, 1244, 1213, 1178, 1151, 1111, 1084, 1059, 1038, 1018, 970, 910, 879, 854, 816, 735, 694, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 25°C): δ = 2.36 (s, 3H, Ts-CH_3), [2.59 (t, $^3J_{H,H}$ = 13.5 Hz, 1H), 3.56 (dd, $^3J_{H,H}$ = 13.5, 3.5 Hz, 1H)] (*p*-O_2N-C_6H_4-CH_2-), 3.88-3.95 (m, 1H, Ts-C-CH<), [4.03 (t, $^2J_{H,H}$ = 9.0 Hz, 1H), 4.31 (t, $^2J_{H,H}$ = 8.5 Hz, 1H)] (lactone -OCH_2-), [4.75, 4.88] (ddd, $^2J_{H,H}$ = 12.5 Hz, $^3J_{H,H}$ = 6.5, 1.0 Hz, 2H, -CH=CH-CH_2-), 6.15 (dt, $^3J_{H,H}$ = 16.0, 7.0 Hz,

1H, Ph-CH=C*H*-), 6.65 (d, $^{3}J_{H,H}$ = 16.0 Hz, 1H, Ph-CH=), 7.25-7.36 (m, 9H, *m*-NO_2Ar, *m*-SO_2Ar, 5× Ph-H), 8.02 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H, *o*-SO_2Ar), 8.14 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H, *o*-NO_2Ar),; ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 21.8 (Ts-CH_3), 35.4 (*p*-O_2N-C_6H_4-*C*H_2-), 42.7 (Ts-C-*C*H<), 67.8 (Ph-CH=CH-*C*H_2O-), 70.0 (lactone -OCH_2-), 78.1 (-OCO-*C*(Ts)-COO-), 120.5 (3°), 124.3 (3°), 126.8 (3°), 128.8 (3°), 129.3 (3°), 129.6 (3°), 132.1 (3°), 132.3 (4°), 135.4 (4°), 137.1 (3°), 144.2 (4°), 146.7 (4°), 147.3 (4°), [162.1, 166.9] (2× C=O); *m/z* (FAB) 536 $[M+H]^+$, 248, 117 (Found: $[M+H]^+$, 536.1364. $C_{28}H_{25}NO_8S$ requires $[M+H]^+$, 536.1379) (Found: C, 62.59; H, 4.62; N, 2.59. $C_{28}H_{25}NO_8S$ requires C, 62.79; H, 4.70; N, 2.62%).

(±)-(Allyl)(5-(trimethylsilyl)pent-2-en-4-yn-1-yl)-2-(toluene-4-sulfonyl)malonate (5h): Sodium hydride (80 mg, 2.0 mmol), (*E*)-5-(trimethylsilyl)pent-2-en-4-ynyl (toluene-4-sulfonyl)acetate **1g** (351 mg, 1.0 mmol) and allyl *p*-nitrophenyl carbonate **7c** (223 mg, 1.0 mmol) were employed in general procedure **3**, *with the following additions:* Rigorous care was taken to exclude moisture from the reaction mixture, otherwise desilylation of the product was observed. **1g** was azeotropically dried from PhMe immediately prior to use. The EtOAc solution of the crude product was concentrated under reduced pressure *without heating.* Chromatography (40:957:3 EtOAc:PhMe:NEt_3) gave **5h** (73 mg, 17%) as a colourless oil; R_f 0.32 (5:95 EtOAc:PhMe); ν_{max} (film) 2957, 2137, 1742, 1597, 1449, 1337, 1250, 1151, 1082, 950, 843, 814, 760, 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.18 (s, 9H, -$Si(CH_3)_3$), 2.45 (3H, s, Ts-CH_3), 4.66 (4H, d, $^{3}J_{H,H}$ = 6.5 Hz, 2 × -CH_2-O-), 4.98 (s, 1H, -CH(Ts)-), 5.27 (d with fine struct., $^{3}J_{H,H}$ = 10.5 Hz, 1H, H*H*C=CH- *cis* to H), 5.34 (d with fine struct., $^{3}J_{H,H}$ = 17.0 Hz, 1H, *H*HC=CH- *trans* to H), 5.70 (d, $^{3}J_{H,H}$ = 16.0 Hz, 1H, ≡C-C*H*=CH-), 5.80-5.89 (m, 1H, H_2C=C*H*-), 6.07 (dt, $^{3}J_{H,H}$ = 16.0, 6.5 Hz, 1H, ≡C-CH=C*H*-), 7.35 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H, *m*-SO_2-Ar), 7.83 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H, *o*-SO_2-Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = -0.2 (-$Si(CH_3)_3$), 21.8 (Ts-CH_3), [66.0 and 67.5] (2 × -CH_2-O-), 74.5 (-*C*H(Ts)-), 97.1 (Me_3Si-*C*≡), 101.9 (Me_3Si-C≡*C*-), 114.8 (3°), 119.0 (=CH_2), [129.6, 130.2 and 130.4] (3°), 134.1 (4°), 135.2 (3°), 146.1 (4°), 160.5 (2 × C=O); *m/z* (-ve ESI) 433 $[M-H]^-$, 361 (Found: 433.1128. $C_{21}H_{26}O_6SSi$ requires $[M-H]^-$ 433.1147) (Found: C, 58.31; H, 6.17. $C_{21}H_{26}O_6SSi$ requires C, 58.04; H, 6.03%).

Synthesis of Monorearrangement products **6**

Tosylmalonate monorearrangement product (*yield)*	Structure
6a (95%)	
6b (81%)	
6c (79%)	
6d (84%)	
6e (66%)	
6f (82%)	

6g (29%)	
6h (26%)	

General procedure (4) for the synthesis of tosylmalonate monorearrangement products 6: To *desired 2-(toluene-4-sulfonyl)malonate bis(allyl) ester* **5a-h** (1.0 equiv) was added potassium acetate (oven-dried, 0.1 equiv). The reaction vessel was purged with N_2, then CH_2Cl_2 (0.1M) was introduced via syringe. *N,O*-bis(trimethylsilyl)acetamide (distilled, 1.0 or 2.0 equiv) was introduced via syringe. The reaction mixture was stirred at rt for 16h (unless otherwise specified), then concentrated under reduced pressure and purified by column chromatography (EtOAc-hexane or EtOAc-petrol, with basic additives as necessary) to give *desired (toluene-4-sulfonyl)monoester* **6.**

(2*E*,4*E*)-Hexa-2,4-dienyl 3-(4-methoxyphenyl)-2-(toluene-4-sulfonyl)pent-4-enoate (6a): (±)-((2*E*,4*E*)-hexa-2,4-dienyl)(4-methoxycinnamyl)-2-(toluene-4-sulfonyl)malonate **5a** (64 mg, 0.132 mmol), potassium acetate (≈ 1 mg, 0.013 mmol) and *N,O*-bis(trimethylsilyl)acetamide (33 µl, 0.132 mmol) were employed in general procedure 4, *with the following additions:* The reaction temperature was 0 °C, the reaction time was 2 h; TLC indicated reaction completion. Chromatography (125:872:3 EtOAc:hexane:NEt_3) gave **6a** (55 mg, 95%) as a colourless oil; R_f 0.40 (20:80 EtOAc:hexane); ν_{max} (film) 2935 1736 1608 1597 1511 1443 1375 1323 1304 1247 1178 1141 1082 1032 990 923 814 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ =1.76 (t, $^3J_{H,H}$ = 7.0 Hz, 3H, =CH-CH_3, 2 × diast.), 2.37 (s, 3H, Ts-CH_3, min. diast.), 2.44 (s, 3H, Ts-CH_3, maj. diast.), 3.73 (s, 3H, -OCH_3, maj. diast.), 3.75 (s, 3H, -OCH_3, min. diast.), 3.99-4.19 (m, 3H min. diast + 1H

maj. diast., -O-CH_2- min. diast & MeO-C_6H_4C*H*< 2 × diast.), 4.40 (d, $^3J_{H,H}$ = 11.5 Hz, 1H, -OC(O)-C(Ts)*H*-, maj. diast.), 4.42 (d, $^3J_{H,H}$ = 10.5 Hz, 1H, -OC(O)-C(Ts)*H*-, min. diast.), 4.56-4.61 (m, 1H, -O-C*H*H-, maj, diast.), 4.96-5.04 (m, 1H, -O-CH*H*-, maj, diast.), 5.10 (d, $^3J_{H,H}$ = 17.0 Hz, 1H, H*H*C=CH-, *trans* to H, 2 × diast.), 5.14 (d, $^3J_{H,H}$ = 10.5 Hz, 1H, *H*HC=CH-, *cis* to H, 2 × diast.), 5.29-6.25 (5H, m, 3° olefinic H), 6.69 (dt, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, *m*-MeO-Ar, min. diast.), 6.76 (dt, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, *m*-MeO-Ar, maj. diast.), 6.99 (dt, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, *o*-MeO-Ar, min. diast.), 7.03 (dt, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, *o*-MeO-Ar, maj. diast.), 7.12 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *m*-SO_2-Ar, min. diast.), 7.31 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-SO_2-Ar, maj. diast.), 7.40 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *o*-SO_2-Ar, min. diast.), 7.79 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2-Ar, maj. diast.); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 18.1 (=CH-*C*H_3), 21.6 & 21.7 (Ts-CH_3, 2 × diast.), 48.3 & 48.4 (MeO-C_6H_4-*C*(H)<, 2 × diast.), 55.1 & 55.1 (-O-CH_3, 2 × diast.), 66.2 & 66.7 (-O-CH_2-, 2 × diast.), 75.0 & 75.5 (-OC(O)-*C*(Ts)H-, 2 × diast.), 113.9 (3°), 114.0 (3°), 114.1 (3°), 117.6 & 117.4 (=CH_2, 2 × diast.), 122.2 (3°), 122.4 (3°), 127.9 (3°), 128.7 (3°), 129.0 (3°), 129.2 (3°), 129.3 (3°), 129.4 (3°), 129.7 (3°), 129.7 (4°), 130.2 (3°), 131.1 (4°), 131.4 (3°), 131.8 (3°), 134.9 (4°), 135.4 (3°), 135.9 (4°), 136.0 (3°), 136.7 (3°), 137.0 (3°), 144.4 &145.3 (4° SO_2-Ar, 2 × diast.), 158.7 & 158.8 (4° MeO-Ar, 2 × diast.), 164.9 & 165.0 (C=O, 2 × diast.); *m/z* (-ve ESI) 439 $[M-H]^-$, 351, 281, 226 (Found: 903.3212. $C_{25}H_{28}O_5S$ requires $[2M+Na]^+$ 903.3206).

(2*R,3*S**)-Cinnamyl 3-(4-methoxyphenyl)-2-(toluene-4-sulfonyl)pent-4-enoate (6b):** (±)-(cinnamyl)(4-methoxycinnamyl)-2-(toluene-4-sulfonyl)malonate **5b** (288 mg, 0.553 mmol), potassium acetate (≈ 5 mg, 0.06 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (135 µl, 0.55 mmol) were employed in general procedure 4, *with the following additions:* The reaction time was 2 h. Chromatography (5:95 to 12:88 EtOAc:petrol) gave **6b** (213 mg, 81%) as a pale yellow oil and as an inseparable mixture of diastereoisomers. Recrystallisation from hexane/EtOAc gave **6b** as a single diastereoisomer, relative configuration confirmed by x-ray crystallographic analysis; mp 116–118 °C; R_f 0.16 (20:80 EtOAc:petrol); ν_{max} (film) 3080, 3059, 3028, 1738, 1637, 1608, 1597, 1512, 1495, 1448, 1377, 1323, 1306, 1279, 1259, 1178, 1142, 1084, 1032, 966, 918, 862, 816, 779, 729, 708, 692, 668, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 2.38 (3H, s, Ts-CH_3), 3.62 (3H, s, Ar-OCH_3), 4.05 (dd, $^3J_{H,H}$ = 11.5, 8.5 Hz, 1H, MeO-C_6H_4-C*H*<), 4.28 (ddd, $^3J_{H,H}$ = 12.5, 7.0 Hz, $^4J_{H,H}$ =1.0 Hz, 1H, -C*H*HO-), 4.37 (ddd, $^3J_{H,H}$ = 12.5, 7.0 Hz, $^4J_{H,H}$ =1.0 Hz, 1H, -CH*H*O-), 4.46 (d, $^3J_{H,H}$ = 11.5 Hz, 1H, -OCO-C(H)Ts-), 5.13 (d, $^3J_{H,H}$ = 17.5 Hz, 1H, *trans* -CH=CH_2), 5.16 (d, $^3J_{H,H}$ = 9.5 Hz, 1H, *cis* -CH=CH_2), 5.66 (dt,

$^{3}J_{H,H}$ = 16.0, 7.0 Hz, 1H, Ph-CH=C*H*-), 6.17 (ddd, $^{3}J_{H,H}$ = 18.0, 9.0, 7.5 Hz, 1H, -C*H*=CH_2), 6.33 (d, $^{3}J_{H,H}$ = 16.0 Hz, 1H, Ph-CH=), 6.73 (dt, $^{3}J_{H,H}$ = 9.5, 2.5 Hz, 2H, *o*-MeOAr), 7.06 (dt, $^{3}J_{H,H}$ = 9.5, 2.5 Hz, 2H, *m*-MeOAr), 7.23-7.34 (m, 7H, other Ar-H), 7.80 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H, *o*-SO_2Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 21.7 (Ts-CH_3), 48.4 (MeO-C_6H_4-*C*H<), 55.1 (Ar-OCH_3), 66.3 (-CH_2O-), 75.6 (-OCO-*C*(Ts)H-), 114.2 (3° MeOAr), 117.7 (=CH_2), 121.7 (Ph-CH=*C*H-), [126.6, 128.2, 128.6] (3° Ph), 129.1 (3° MeOAr), 129.5 (3° -SO_2Ar), 129.7 (3° -SO_2Ar), 131.1 (4° MeOAr), 134.8 (Ph-CH=), 135.0 (4° -SO_2Ar), 135.9 (4° Ph), 137.1 (-*C*H=CH_2), 145.4 (4° -SO_2Ar), 158.8 (4° MeOAr), 165.0 (C=O); *m/z* (CI) 494 $[M+NH_4]^+$, 450, 340, 334, 279, 224, 174, 161, 147, 134 $[C_9H_{10}O]^+$, 117 $[C_9H_9]^+$, 101 (Found: $[M+NH_4]^+$, 494.1983. $C_{28}H_{28}O_5S$ requires $[M+NH_4]^+$, 494.2001).

Cinnamyl (*E*)-2-(toluene-4-sulfonyl)-3-vinylhex-4-enoate (6c): (±)-(cinnamyl)((2*E*,4*E*)-hexa-2,4-dienyl)-2-(toluene-4-sulfonyl)malonate **5c** (567 mg, 1.25 mmol), potassium acetate (12 mg, 0.13 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (300 µl, 1.25 mmol) were employed in general procedure 4. Chromatography (15:85 EtOAc:petrol) gave **6c** (407 mg, 79%) as a pale yellow oil and as an inseparable mixture of diastereoisomers; R_f 0.31 (20:80 EtOAc:petrol); ν_{max} (film) 3028, 3060, 3028, 1739, 1637, 1597, 1495, 1448, 1379, 1325, 1306, 1213, 1146, 1084, 966, 924, 847, 816, 744, 708, 694, 660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = [1.56, 1.67] (dd, $^{3}J_{H,H}$ = 6.5 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 3H, =CH-C*H*$_3$, 2× diast.), [2.35, 2.36] (s, 3H, Ts-CH_3, 2× diast.), 3.51-3.62 (m, 1H, H_3C-CH=CH-C*H*(CH=CH_2)-, 2× diast.), 4.07 (d, $^{3}J_{H,H}$ = 9.5 Hz, 1H, -OCO-CH(Ts)-, 2× diast.), [4.61 (ddd, $^{3}J_{H,H}$ = 6.5, 2.5 Hz, $^{4}J_{H,H}$ = 1.5 Hz), 4.64 (ddd $^{3}J_{H,H}$ = 6.5, 1.0 Hz, $^{4}J_{H,H}$ = 1.0 Hz)] (2H, -CH_2O-, 2× diast.), [5.04, 5.16] (dt, $^{3}J_{H,H}$ = 10.5 Hz, $^{4}J_{H,H}$ = 1.0 Hz, 1H, *cis* -CH=C*H*$_2$, 2× diast.), [5.09, 5.16] (dt, $^{3}J_{H,H}$ = 17.0 Hz, $^{4}J_{H,H}$ = 1.0 Hz, 1H, *trans* -CH=C*H*$_2$, 2× diast.), [5.33 (ddq, $^{3}J_{H,H}$ = 15.5, 8.5 Hz, $^{4}J_{H,H}$ = 1.5 Hz), 5.38 (ddq, $^{3}J_{H,H}$ = 14.0, 7.5 Hz, $^{4}J_{H,H}$ = 1.5 Hz)] (1H, H_3C-CH=C*H*-, 2× diast.), [5.53 (dqd, $^{3}J_{H,H}$ = 15.0, 6.5 Hz, $^{4}J_{H,H}$ =1.0 Hz), 5.58 (dqd, $^{3}J_{H,H}$ = 14.5, 6.5 Hz, $^{4}J_{H,H}$ = 1.0 Hz)] (1H, H_3C-C*H*=, 2× diast.), [5.73, 5.90] (ddd, $^{3}J_{H,H}$ = 17.5, 10.0, 7.5 Hz, 1H, H_2C=C*H*-, 2× diast.), [6.05, 6.08] (dt, $^{3}J_{H,H}$ = 16.0, 6.5 Hz, 1H, Ph-CH=C*H*-, 2× diast.), [6.57, 6.58] (dt, $^{3}J_{H,H}$ = 16.0 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 1H, Ph-CH=, 2× diast.), 7.25-7.36 (m, 7H, other Ar-H), [7.75, 7.76] (dd, $^{3}J_{H,H}$ = 8.5 Hz, $^{4}J_{H,H}$ = 2.0 Hz, 2H, *o*-SO_2Ar, 2× diast.); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = [18.1, 18.0] (=CH-*C*H_3, 2× diast.), 21.7 (Ts-CH_3, 2× diast.), 46.3 (H_3C-CH=CH-*C*H(CH=CH_2)-, 2× diast.), 46.3 (H_3C-CH=CH-*C*H(CH=CH_2)-, 2× diast.), [66.4, 66.5] (-CH_2O-, 2× diast.), [74.3, 74.4] (-OCO-*C*H(Ts)-, 2× diast.), 117.4, 117.5,

121.9, 126.7, 127.4, 128.0, 128.3 (×2), 128.7, 129.2, 129.3, 129.4, 129.5, 129.6, 135.1, 135.2, 135.6, 135.7, 136.0, 136.2, 145.2, 145.3, 165.2 (C=O); *m/z* (CI) 428 $[M+NH_4]^+$, 268, 255, 197, 174, 156, 139, 134 $[C_9H_{10}O]^+$, 117 $[C_9H_9]^+$, 95 (Found: $[M+NH_4]^+$, 428.1897. $C_{24}H_{26}O_4S$ requires $[M+NH_4]^+$, 428.1896).

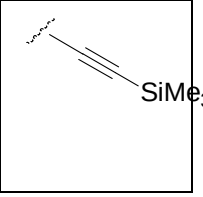
(*E*)-Pent-2-enyl 3-phenyl-2-(toluene-4-sulfonyl)pent-4-enoate, (6d) and Cinnamyl 3-ethyl-2-(toluene-4-sulfonyl)pent-4-enoate (6d'): (±)-(cinnamyl)((2*E*)-pent-2-enyl)-2-(toluene-4-sulfonyl)malonate **5d** (250 mg, 0.565 mmol), potassium acetate (5 mg, 0.06 mmol), and *N*,*O*-bis(trimethylsilyl)acetamide (0.275ml, 1.13 mmol) were used in general procedure 4, *with the following additions*: The solvent was PhMe (5 mL), the reaction temperature was 55 °C and the reaction time was 4 h. Chromatography (15:85 EtOAc:petrol) gave **6d** and **6d'** (190 mg total, 84%) as a yellow oil and as an inseparable mixture of regio- and diastereoisomers. **6d** was the major regioisomer in a ratio **6d**:**6d'** 3:1; R_f 0.34 (20% EtOAc–petrol); ν_{max} (film) 3082, 3062, 3030, 1739, 1671, 1639, 1597, 1493, 1454, 1415, 1401, 1379, 1327, 1306, 1279, 1205, 1182, 1146, 1084, 1018, 970, 926, 814, 760, 746, 702, 663 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 0.80-1.05 (m, 3H, -CH_2CH_3), 1.11-1.59 (m, 2H, H_3C-CH_2, 2× diast. of **6d'**), [1.93, 2.09] (t, $^3J_{H,H}$ = 7.0 Hz, 2H, H_3C-CH_2-, 2× diast. of **6d**), [2.33, 2.35, 2.38, 2.46] (s, 3H, Ts-CH_3 for 2× diast. each of **6d', 6d**), 2.75-2.89 (m, 1H, H_3C-CH_2-CH< for **6d'**), 3.49-3.72 (m, 1H, SO_2CH< for **6d'**), 4.00-4.24 (m, 2H, -SO_2CH<, Ph-CH< for **6d**), [4.50, 4.54, 4.68] (d, $^3J_{H,H}$ = 6.5 Hz, 2H, -OCH_2- for **6d'**, **6d**), 4.92-6.25 (m, 5H, olefinic **6d'**, **6d**), [6.54, 6.60] (d, $^3J_{H,H}$ = 16.5 Hz, 1H for 6d', Ph-CH=, 2× diast. of **6d'**), 7.11-7.42 (m, 7H, other Ar-H), 7.78-7.84 (m, 2H, *o*-SO_2Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = [11.0, 11.2] (H_3C-CH_2- for 2× diast. of **6d'**), [13.0, 13.1] (H_3C-CH_2- for 2× diast. of **6d**), [21.6, 21.7] (Ts-CH_3), [25.2, 25.3] (H_3C-CH_2-), [44.6, 44.8] (H_3C-CH_2-CH< for 2× diast. of **6d'**), [49.3, 49.3] (Ph-CH< for 2× diast. of **6d**), [66.3, 66.5, 67.0] (-CH_2O-), [74.3, 74.9, 75.0, 75.1] (-SO_2CH< for 2× diast. of **6d'**, **6d**), 117.8, 117.9, 118.5, 118.9, 121.5, 121.9, 126.7, 127.3, 127.4, 128.0, 128.3, 128.4, 128.6, 128.7, 128.8, 129.3, 129.5, 129.6, 129.8, 135.1, 135.3, 135.5, 136.0, 136.0, 136.5, 136.6, 136.9, 138.0, 138.5, 139.1, 139.3, [144.6, 145.2, 145.3, 145.4] (4° -SO_2Ar for 2× diast. of **6d'**, **6d**), [164.9, 165.0, 165.3, 165.7] (C=O for 2× diast. of **6d'**, **6d**); *m/z* (CI) 416 $[M+NH_4]^+$, 372 $[M+NH_4-CO_2]^+$, 348, 316, 304, 262, 256, 237 (Found: $[M+NH_4]^+$, 416.1896. $C_{23}H_{26}O_4S$ requires $[M+NH_4]^+$, 416.1896).

Allyl 3-phenyl-2-(toluene-4-sulfonyl)pent-4-enoate (6e): (±)-(allyl)(cinnamyl)-2-(toluene-4-sulfonyl)malonate **5e** (1.14 g, 2.76 mmol), potassium acetate (27 mg, 0.28 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (1.34 mL, 5.52 mmol, 2.0 equiv) were used in general procedure 4, *with the following additions*: The solvent was PhMe (55 mL), the reaction temperature was 110 °C and the reaction time was 16 h. Chromatography (2:98→12.5:87.5 EtOAc:petrol) gave **6e** (670 mg, 66%) as a pale yellow oil and as an inseparable mixture of diastereoisomers; R_f 0.26 (20% EtOAc–petrol); ν_{max} (film) 3084, 3062, 3030, 1741, 1639, 1597, 1493, 1454, 1327, 1290, 1279, 1205, 1146, 1084, 989, 928, 858, 816, 760, 744, 702, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = [2.39 (min. diast.), 2.48 (maj. diast.)] (s, 3H, Ts-CH_3, 2× diast.), [4.01-4.24, 4.49-4.65] (m, 4H, -OCH_2-, -SO_2CH<, H_2C=CH-C(Ph)*H*-, 2× diast.), 4.95-5.42 (m, 4H, both -CH=CH_2, 2× diast.), 5.81-5.97 (m, 1H, H_2C=C*H*-C(Ph)H-, 2× diast.), 6.13-6.24 (m, 1H, H_2C=C*H*-CH_2-, 2× diast.), 7.11-7.41 (m, 7H, other Ar-H), [7.77 (min. diast.), 7.83 (maj. diast.)] (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = [22.0, 22.1] (Ts-CH_3, 2× diast.), [49.7, 49.8] (H_2C=CH-*C*(Ph)H-, 2× diast.), [66.7, 67.2] (-OCH_2-, 2× diast.), [75.3, 75.8] (-SO_2CH<, 2× diast.), 118.2 (2°), 118.4 (2°), 119.3 (2°), 119.5 (2°), 119.6 (2°), 119.8 (2°), 127.1 (3°), 127.7 (3°), 127.9 (3°), 128.4 (3°), 128.8 (3°), 129.0 (3°), 129.1 (3°), 129.2 (3°), 129.8 (×2) (3°), 129.9 (3°), 130.2 (3°), 131.1 (3°), 131.4 (3°), 131.5 (3°), 132.1 (3°), 135.3 (4°), 136.4 (4°), 137.0 (3°), 137.1 (3°), 138.2 (4°), 139.6 (4°), 145.0 (4°), 145.9 (4°), [165.2, 165.3] (C=O, 2× diast.); *m/z* (CI) 388 $[M+NH_4]^+$, 312, 214, 174, 61, 44 (Found: $[M+NH_4]^+$, 388.1576. $C_{21}H_{22}O_4S$ requires $[M+NH_4]^+$, 388.1583) (Found: C, 67.97; H, 5.86. $C_{21}H_{22}O_4S$ requires C, 68.08; H, 5.99%).

(*E*)-5-(Trimethylsilyl)pent-2-en-4-ynyl 3-phenyl-2-(toluene-4-sulfonyl)pent-4-enoate (6f): (±)-(cinnamyl)(5-trimethylsilanylpent-2-en-4-ynyl)-2-(toluene-4-sulfonyl)malonate **5f** (143 mg, 0.279 mmol, 1.0 equiv), potassium acetate (3 mg, 0.028 mmol, 0.1 equiv) and *N*,*O*-bis(trimethylsilyl)acetamide (70 μL, 0.279 mmol, 1.0 equiv) were used in general procedure 4. Chromatography (20:80 EtOAc:petrol) gave **6f** (102 mg, 82%) as a yellow oil and as an inseparable mixture of diastereoisomers; R_f 0.32 (20% EtOAc–petrol); ν_{max} (film) 3064, 3032, 2179, 2135, 1743, 1637, 1597, 1493, 1454, 1406, 1377, 1329, 1306, 1277, 1252, 1205, 1184, 1146, 1084, 987, 951, 926, 847, 760, 739, 702, 654 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.20 (s, 9H, -$Si(CH_3)_3$), [2.37, 2.46] (s, 3H, Ts-CH_3), 4.05-4.22 (m, 1H + 2H for 1st diast., Ph-CH< for 2× diast., -OCH_2- for 1st diast.), [4.47 (d, $^3J_{H,H}$ = 8.0 Hz), 4.49 (d, $^3J_{H,H}$ = 7.0 Hz)] (1H, -SO_2-CH<, 2× diast.), 4.60 (d, $^3J_{H,H}$ = 6.0 Hz, 2H for 2nd diast., -OCH_2-), 5.05-5.195 (m, 2H, -CH=CH_2), [5.29 (1st

diast.), 5.73 (2nd diast.)] (d, $^3J_{H,H}$ = 16.0 Hz, 1H, -OCH_2-CH=C*H*-), [5.54 (1st diast.), 6.07 (2nd diast.)] (dt, $^3J_{H,H}$ = 16.0, 6.0 Hz, 1H, -OCH_2-C*H*=), [5.89 (ddd, $^3J_{H,H}$ = 18.0, 9.0, 8.0 Hz, 1st diast.), 6.18 (ddd, $^3J_{H,H}$ = 18.0, 9.0, 7.5 Hz, 2nd diast.)] (1H, H_2C=C*H*-), [7.08-7.38 (m, other Ar-H), 7.79 (d, $^3J_{H,H}$ = 8.0 Hz, *o*-SO_2Ar for 1 diast.)] (9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = –0.2 (-Si(CH_3)$_3$) , [21.8, 21.7] (Ts-CH_3), [49.3, 49.3] (Ph-CH<), [64.9 (1st diast), 65.4 (2nd diast.)] (-OCH_2-), [74.8, 75.3] (-SO_2CH<), [96.6, 96.7] (-OCH_2-CH=CH-C≡*C*-), 102.2 (-OCH_2-CH=CH-*C*≡), [113.8 (1st diast.), 114.3 (2nd diast.)] (-OCH_2-CH=*C*H-), [118.1, 117.9] (-CH=*C*H_2) , 127.4 (3°), 127.7 (3°), 127.9 (3°), 128.3 (3°), 128.6 (3°), 128.7 (3°), 128.9 (3°), 129.4 (3°), 129.6 (3°), 129.7 (3°), [134.8, 135.8] (*i*-SO_2Ar) [135.6 (1st diast.), 136.0 (2nd diast.)] (-OCH_2-*C*H=), [136.4 (1st diast.), 136.6 (2nd diast.)] (H_2C=*C*H-), [137.8, 139.0] (*i*-Ph), [144.8, 145.6] (*p*-SO_2Ar), 164.7 (×2, C=O); *m/z* (CI) 484 $[M+NH_4]^+$, 467 $[M+H]^+$, 311, 182, 157, 141, 117, 91 (Found: $[M+NH_4]^+$, 484.1966. $C_{26}H_{30}O_4SSi$ requires $[M+NH_4]^+$, 484.1978).

***p*-Nitrocinnamyl 3-phenyl-2-(toluene-4-sulfonyl)pent-4-enoate (6g) and Cinnamyl 3-(4-nitrophenyl)-2-(toluene-4-sulfonyl)pent-4-enoate (6g'):** (±)-1-cinnamyl 3-(*E*)-3-(4-nitrophenyl)allyl 2-(toluene-4-sulfonyl)malonate **5g** (255 mg, 0.476 mmol), potassium acetate (5 mg, 0.048 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (116 μL, 0.476 mmol, 1.0 equiv) were used in general procedure 4. Chromatography (30:70 EtOAc:petrol) gave **6g** and **6g'** (67 mg total, 29%) as a yellow gum and as an inseparable mixture of regio- and diastereoisomers. **6g** was the major regioisomer in a ratio **6g**:**6g'** 3:1; R_f 0.44 (30% EtOAc–petrol); ν_{max} (film) 3064, 3030, 3007, 1741, 1597, 1518, 1493, 1454, 1377, 1344, 1327, 1304, 1290, 1205, 1184, 1146, 1111, 1084, 1016, 972, 914, 860, 814, 733, 702, 665, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = [2.36, 2.37, 2.44, 2.46] (s, 3H, Ts-CH_3), [4.06 (dd, $^3J_{H,H}$ = 11.0, 4.0 Hz), 4.25-4.12 (m)] (1H, Ts-CH-C*H*<), [4.54 (d, $^3J_{H,H}$ = 4.0 Hz), 4.57 (d, $^3J_{H,H}$ = 3.5 Hz), 4.59 (d, $^3J_{H,H}$ = 4.0 Hz)] (1H, Ts-CH<), [4.35 (dd, $^2J_{H,H}$ = 13.5 Hz, $^3J_{H,H}$ = 6.0 Hz), 4.45 (dd, $^2J_{H,H}$ = 13.5 Hz, $^3J_{H,H}$ = 6.0 Hz), 4.93-4.74 (m)] (2H, -OCH_2-), 5.15 (1H, d, $^3J_{H,H}$ = 17.0 Hz, *trans* -CH=CH_2), [5.06 (d, $^3J_{H,H}$ = 10.0 Hz), 5.18 (d, $^3J_{H,H}$ = 9.5 Hz)] (1H, *cis* -CH=CH_2), [5.36-5.344 5.79-5.91, 5.97-5.99] (m, 1H, NO_2Ar-CH=C*H*- and Ph-CH=C*H*-), [5.91-5.94], 6.08-6.20 (m, 1H, -C*H*=CH_2), 6.42 (d, $^3J_{H,H}$ = 16.0 Hz, 1H **6g** maj. diast. and **6g'** min. diast., NO_2Ar-C*H*= and Ph-C*H*=), 6.44 (d, $^3J_{H,H}$ = 16.0 Hz, 1H **6g'** maj. diast., Ph-C*H*=), 6.79 (d, $^3J_{H,H}$ = 16.0 Hz, 1H **6g** min. diast., NO_2Ar-C*H*=), [7.08-7.44 (m), 7.54 (d, $^3J_{H,H}$ = 8.5 Hz), 7.84 (d, $^3J_{H,H}$ = 8.0 Hz)] (11H, *o*-SO_2Ar, *m*-NO_2Ar, *m*-SO_2Ar, Ph-H), [8.20, 8.22] (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *o*-NO_2Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 21.6, 21.8, 22.7, 29.7, 49.4, 49.5, 62.0, 62.5, 65.4, 65.9, 75.0, 75.3, 77.3, 117.8, 118.2, 123.7, 123.8, 123.9, 124.1, 124.3, 126.7,



127.0, 127.2, 127.3, 127.4, 127.5, 128.0, 128.4, 128.6, 128.7, 128.9 (×2) , 129.4, 129.6, 129.8, 131.5, 131.8, 132.0, 132.2, 134.9, 136.0, 136.6 (×2) , 137.6, 139.2, 139.3, 142.1, 142.3, 142.4, 142.5, 144.7, 145.6, 147.3, 164.9; *m/z* (CI) 509 $[M+NH_4]^+$, 437, 419, 293, 236, 219 (Found: $[M+NH_4]^+$, 509.1748. $C_{27}H_{25}NO_6S$ requires $[M+NH_4]^+$, 509.1746).

(±)-(*E*)-5-(Trimethylsilyl)pent-2-en-4-ynyl 2-(toluene-4-sulfonyl)pent-4-enoate (6h): (±)-(Allyl)(5-(trimethylsilyl)pent-2-en-4-yn-1-yl)-2-(toluene-4-sulfonyl) malonate **6h** (43 mg, 0.099 mmol), potassium acetate (1 mg, 0.001 mmol) and *N,O*-bis(trimethylsilyl)acetamide (49 µL, 0.198 mmol, 2.0 equiv) were used in general procedure 4, *with the following additions*: The reaction was performed under conditions of microwave acceleration, the reaction temperature was 130 °C and the reaction time was 5 min. Chromatography (10:90 EtOAc:hexane) gave **6h** (10 mg, 26%) as a colourless oil; R_f 0.24 (10% EtOAc-hexane); ν_{max} (film) 2136, 1743, 1643, 1597, 1440, 1376, 1328, 1305, 1250, 1169, 1147, 1084, 951, 924, 843, 814, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.19 (s, 9H, -Si(CH_3)$_3$), 2.46 (s, 3H, Ts-CH_3), 2.69 (ddd, $^2J_{H,H}$ = 14.0 Hz, $^3J_{H,H}$ = 11.5, 7.5 Hz, 1H, H_2C=CH-CH*H*-), 2.78-2.85 (m, 1H, H_2C=CH-C*H*H-), 3.98 (dd, $^3J_{H,H}$ = 11.5, 4.0 Hz, 1H, -OC(O)-CH(Ts)-), 4.51 (ddd, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 5.0, 2.0 Hz, 1H, -CH*H*O-), 4.56 (ddd, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 5.0, 1.5 Hz, 1H, -C*H*HO-), 5.09 (dd, $^3J_{H,H}$ = 10.0 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H, *cis* -CH=CH_2), 5.11 (dd, $^3J_{H,H}$ = 17.0 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, *trans* -CH=CH_2), 5.62 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, ≡C-C*H*=CH-), 5.60-5.71 (m, 1H, H_2C=C*H*-), 5.97 (dt, $^3J_{H,H}$ = 16.0, 6.0 Hz, 1H, ≡C-CH=C*H*-), 7.36 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-SO_2Ar), 7.73 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-SO_2Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = –0.2 (-Si(CH_3)$_3$), 21.7 (Ts-CH_3), 30.8 (H_2C=CH-CH_2-), 65.2 (-CH_2O-), 70.1 (-OCO-*C*H(Ts)-) , 96.9 (Me_3Si-*C*≡), 102.0 (Me_3Si-C≡*C*-), 114.4 (3°), 119.2 (=CH_2) , 129.4 (3°), 129.8 (3°), 131.7 (3°), 134.0 (4°), 135.8 (3°), 145.6 (4°), 165.0 (C=O); *m/z* (CI) 413 $[M+Na]^+$, 391 $[M+H]^+$, 235, 137 (Found: 413.1211. $C_{20}H_{26}O_4SSi$ requires $[M+Na]^+$ 413.1213).

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